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THE SPECTRA OF INTERSTELLAR MOLECULES

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ABSTRACT

This review considers the spectroscopic observations which have led to the identification of more than 50 molecules in the interstellar medium. Although it concentrates on the results of radio studies, mainly because these have up to now been the most revealing, optical and infrared discoveries are also reviewed and placed in perspective. The radio data yield information about the very cold regions whereas the infrared data yield information about the warmer regions where stars are forming. Optical emission studies can give information about extremely hot regions near stars and absorption studies give information about the cold regions.

The review begins with a historical introduction to the field followed by a brief overview of the interstellar medium and its relationship with other objects in the Universe in the second section. The third section is devoted to an understanding of the relevant types of spectra, mainly rotational, and salient astronomical details which pertain mainly to radio observations. In the fourth section the optical, radio and infrared spectra of various molecules are individually discussed and some of the most important regions where molecules are found are described. The various interstellar chemical pathways currently being actively studied are discussed in the fifth section. In the final section some of the more important outstanding problems and possible future research avenues are highlighted.

The overall perspective is a spectroscopic one in which the value to chemistry of these studies is deemed as interesting and significant as the value to astronomy.

INTRODUCTION

The black clouds which congregate in the galactic plane have, in recent years, been shown by spectroscopy to harbour vast quantities of molecules which can be used as probes to determine not only the cloud composition but also their physical conditions. As these visibly opaque clouds are the raw material from which stars and planets form, molecular spectroscopy is the medium through which the earliest stages of star formation can for the first time be observed.

Not only has the spectroscopy of molecules in the interstellar medium (ISM) made significant contributions to astronomy through its impact on the Big Bang Theory, the evolution of galaxies and the birth of stars, but it has also had a significant influence on chemistry, physics and biology.

Chemistry has benefited in that the field has facilitated the detection and study of new and exciting molecules, free radicals and ions. In addition, studies of two-body (mainly ion–molecule) processes, surface catalysis and high temperature reactions have been instigated.

As far as physics (or perhaps chemical physics) is concerned the effect has been dramatic. New technical advances have been made specifically to enable us to study the

whole electromagnetic spectrum and sift out the information that interstellar molecules imprint in the radiation reaching the earth. New radiotelescopes, new infrared telescope/spectrometers requiring state of the art detectors and amplifiers have been built. Rocket techniques have also been employed. A whole new field of low temperature physics has developed.

Of course it is inevitable that one should ask the 64 000 dollar question—where molecules are, can life be far behind? Indeed moderately complex molecules have now been found in circumstellar shells, warm clouds, cold dense clouds and, as we all know, on planets. The molecules are for the most part the same but the varied physical conditions may enable some species to be stabilized in one region relative to another. However, it is now clear that these molecular clouds contain all the basic chemical building blocks necessary for the origin of life and that planets, such as the earth, form out of such molecular clouds. The results challenge the traditional view that these molecules (such as amino acids) originally formed in the earth's atmosphere.

Thus the observations have generated some new questions and some new (not necessarily correct) answers about the origins of life.

There can be few readily identifiable subjects which encompass such a wide range of phenomena and draw on the expertise and ingenuity of such a diverse range of scientists.

The first indication of the existence of interstellar matter was the identification of two lines of Ca^+ by Hartmann in 1904 in the spectrum of the double star δ -Orionis. The frequencies of the Ca^+ lines did not exhibit the periodic Doppler shift variations, characteristic of the stellar lines associated with a rotating binary system, whose relative velocity varies in phase with the orbiting motion. The lines were sharp and stationary and sometimes multiplets indicating that several 'clouds' of atoms were strewn along the line of sight to the stellar source. Later other interstellar atomic lines were assigned to Ca, K, Fe and Ti^+ .

The existence of interstellar molecules, although apparently suspected by Eddington (1926) as perhaps lurking in dark and secluded places in space, had to wait some 30 years (Herzberg, 1950, 1980) when Swings and Rosenfeld (1937) assigned a line observed by Dunham (1937) to the molecule CH. Further lines observed by Adams (1941) were assigned by McKellar (1941) to CH and CN. Other lines were identified by Douglas and Herzberg (1941, 1942) who, on the basis of isotopic labelling laboratory experiments, were able to confirm the existence of CH^+ .

Astronomy and spectroscopy have been inextricably bound together ever since Newton originally split the sun's rays into the colours of the spectrum with a prism (Condon and Shortley, 1935; Floyd, 1973) and the most recent results considered here often highlight this (Herzberg, 1980).

These early molecular observations can be seen with hindsight as two steps forward, but the resulting conclusions—perhaps almost subconsciously—were one step back. *All* three molecules: CH, CH^+ and CN are unstable species possessing only transient existence in the laboratory and produced under violent conditions such as those which occur in discharges or high photon fluxes. Thus an impression was formed that only these types of molecule existed in the space between the stars because the conditions were too harsh for the more common terrestrial molecules to survive for any prolonged time.

Eddington (1926) appears to have conjectured that the dark dust clouds might protect molecules such as H_2 by scattering the photodissociating radiation. These dark clouds, studied by Barnard (1927) and the smaller ones by Bok and Reilly (1947) (*see* Dickman, 1977), were impenetrable by these early optical techniques. Nevertheless, these results presented scientists with the data on the basis of which the first theories of interstellar chemical processes were developed by Bates and Spitzer (1951) and McCrea and McNally (1960).

The next phase of the story started rather inconspicuously in the work of Jansky who carried out a systematic study of the origins of terrestrial radio communication interference at the Bell Telephone Laboratories (Jansky, 1933). He identified extra-terrestrial noise from directions in the galactic plane and appears to have proposed a 100 ft mirror antenna to study the problem further (Kraus, 1966). These early studies were followed up by Reber (1939) who built his own 31 ft parabolic dish and produced the first maps of interstellar radio sources (at 160 MHz). He noted that the strongest source was in the direction of Sagittarius towards the galactic centre.

These data were the source of an inspired conjecture by van de Hulst (1945) that the spin-flip transition of the H atom in its electronic ground state should give rise to a signal detectable with the new radio technique (Townes and Schawlow, 1955; Unsöld 1977). The separation between the two H hyperfine states in which the electron and proton spins are either parallel or opposed is 1420 MHz (Ramsey, 1956). This separation, which has its origin in the Fermi contact magnetic term (Hargreaves, 1929, 1930; Fermi 1930; Condon and Shortley, 1935; Tinkham, 1964), was later measured by Nafe, Nelson and Rabi (1947, 1948). This transition not only revolutionized galactic astronomy but also contributed greatly to quantum theory because it indicated the existence of the anomalous value for the electron magnetic moment (Ramsey, 1956) and allowed an accurate value of α the fundamental fine structure constant to be determined.

Perhaps as important as any other point is the realization that non-resonant scattering processes become less important as the frequency decreases. The cross-sections depend on the scattering medium and vary as ω for Mie (particulate) scattering and ω^4 for Raman and Rayleigh (molecular or atomic) scattering. Thus radio waves are essentially unaffected by the foggy patches of dust particles and molecules which congregate in the galactic plane and limit our visibility (optical) to a range of approximately 6000 ly (approximately $\frac{1}{6}$ of the way to the galactic centre).

In particular it allows radio techniques to penetrate the dark dust clouds to which Barnard (1927) had drawn attention in his early studies. The 1420 MHz or 21 cm line was finally detected by Ewen and Purcell (1951) and others (*see* Kraus, 1966) and so for the first time our own galaxy (the Milky Way) became accessible to study and its spiral structure, so long suspected, became apparent. The 21 cm lines are often multiplets due to the Doppler structure associated with transitions from H atom clouds with differing radial velocity distributed along the line of sight. This type of structure was also observed in the earlier optical studies (Munch, 1968).

The observations of CH, CH⁺ and CN together with the development of radio techniques suggested that OH radicals (Townes and Schawlow, 1955) and other molecules such as NH₃, CO and H₂O (Townes, 1957) might be detectable. The prescient discussion by Townes and Schawlow (1955) gives a succinct analysis of the feasibility of molecule detection by radio techniques.

In 1963 OH was detected (Weinreb *et al.*, 1963) and several interesting results were uncovered. Hot compact regions and interstellar masers were detected as were regions of emission as well as absorption. In addition, and perhaps most importantly, OH was sometimes detected in regions of the ISM with little or no H atom emission. This pointed to the possibility that the hydrogen in these regions was indeed molecular and so invisible because H₂ does not possess a readily detectable spectrum.

In 1965, Hoglund and Mezger detected the radio frequency recombination lines of H involving transitions between states with high quantum numbers (i.e. $n = 110 \rightarrow 109$). For $\Delta n = 1$ these transitions follow $\Delta E \sim 2R/(n + \frac{1}{2})^3$ which yields a line at approximately 5008 MHz for $n = 109$.*

* The observed frequency is 5008 MHz and this approximate formula gives 5012 MHz. The correct basic formula is of course $\Delta E = -R[(n + 1)^{-2} - n^{-2}]$.

In this way the scene was set for the critical incision which was made when NH_3 was detected (Cheung *et al.*, 1968, 1969). It is perhaps worth noting that it was this 24 GHz inversion transition, so fundamental to our understanding of quantum mechanical tunnelling (Dennison and Uhlenbeck, 1932, Wollrab 1967) which also initiated the birth of microwave spectroscopy (Cleaton and Williams, 1934) and the beam maser (Gordon, Zeiger and Townes, 1955) and the laser.

There have been several excellent reviews on interstellar molecules in recent years and the field is so wide and varied that almost all of them have been valuable and have managed to present the subject in a fresh and complementary way. Snyder (1972) gives an interesting insight into the early radio discoveries and a comprehensive review with much physical data has been given by Winnewisser, Churchwell and Walmsley (1979). Lang (1980) has given many of the formulae that are the basic tools of the trade. The book by Kraus (1966) gives interesting accounts of the early days of radio astronomy and also deals with radio technology. Useful shorter reviews of interstellar molecules are also given by Rank, Townes and Welch (1971), Solomon (1973), Zuckerman and Palmer (1974) and Winnewisser (1975). The physical conditions of the ISM are discussed in the book by Dyson and Williams (1980) and the reviews by Chaisson (1978) and Turner (1979a). Moran (1976) has discussed interstellar masers. Papers dealing with the chemistry of the ISM have been presented by Herbst and Klemperer (1973) and Solomon and Klemperer (1972). Reviews have been published by Watson (1976), Dalgarno and Black (1976), Dalgarno (1976) and Huntress (1977). Short reviews on interstellar molecules, written for non-specialists, have been given by Gordon and Burton (1979), Gammon (1978) and Kroto (1978).

This review concentrates on the relationship between laboratory studies and astrophysical observations of molecules. Mainly microwave and radio spectra are discussed but some of the recent optical and infrared work has also been covered. It has been written from the perspective of a molecular spectroscopist who views the recent discoveries as being as valuable to molecular science and chemistry in particular as they have been to astronomy. In this way it is hoped that this review overlaps as little as possible with its predecessors, at least in spirit and perspective if not (hopefully) in fact.

THE INTERSTELLAR MEDIUM

The Universe which has dimensions of approximately 10^{10} ly* is roughly 1.3×10^{10} years old and contains some 10^{11} galaxies each containing of the order of 10^{11} stars— 10^{22} in all. The galaxies themselves tend to cluster together in groups of a few to a thousand and the intergalactic distances are of the order of 10^6 ly and intercluster distances about 100×10^6 ly. The galaxies may have irregular or elliptic structure but often have a spiral structure with the stars and matter mainly congregating in a flat disc-shaped volume. In the spiral galaxies stars and planets form out of the interstellar gas and dust that congregates in the galactic plane (Fig. 1). The interstellar material can be considered to flow through a spiral ripple in the overall galactic gravitational field—a density wave which compresses the material from the interarm density of $n_{\text{H}} \sim 10^{-1} - 10^{-2} \text{ cm}^{-3}$ to an average density of $1 - 10 \text{ cm}^{-3}$ in the arm. Here further density inhomogeneities develop into the dense clouds from which stars form. The material is then dispersed as it flows out of the trailing edge of the spiral arm only to take part in the next successive compression phase some 125×10^6 years or half a galactic revolution later.

As far as we can see, since the origin of the universe in the Big Bang it is some 10^{17} seconds (and counting). It was in the very early seconds that H, D, He and the lightest

* Note 1 ly (light year) $\sim 10^{13}$ km.



FIG. 1. The Sombrero Hat Galaxy M104, a spiral galaxy in Virgo seen from an oblique angle. The efficiency with which interstellar matter collecting in the galactic plane scatters the light from the stars in the nucleus is clearly evident (Hale slide).

elements Be, Li and B were formed. Indeed molecular studies promise the possibility of determining such ratios as D/H which are critical in determining the scenario of the first few minutes during which the Universe was born. This may indicate whether the Universe is open (will expand for ever) or closed (will at some future point stop expanding, start to contract and pass through the next cosmic singularity).

The overall interstellar matter/stellar processing scenario is based on an ISM which consists of 70 per cent H, 27 per cent He, 1 per cent dust and 2 per cent the rest, by mass. These numbers may be subject to revision at any time. About 10 per cent of the ISM is processed through the stars of $5 M_{\odot}$ or more which rapidly burn up their H to He and regurgitate most of the nuclear processed material back into the ISM via nova or supernova explosions.

The lighter stars, of about the same mass as the sun ($1 M_{\odot}$ or so) burn up hydrogen much more slowly. They reach a steady state phase soon after their birth and continue for approximately 10 000 million years at which time they have used up much of their H. The core then collapses and the outer shell expands to form a red giant whose hot 2000 K tenuous gaseous envelope has a radius of approximately 1 AU (1 Astronomical Unit \equiv the radius of the earth's orbit) or planetary nebulae with very hot shells approximately 1 ly in radius. Some 15 per cent of the ISM is processed this way and $\frac{2}{3}$ of this (i.e. 10 per cent) is returned to the ISM containing significant amounts of heavier elements.

The heavier elements from C to Fe are believed to have been synthesized in stars during the latter stages of their lives and the very heavy elements in supernova explosions. Some 75 per cent of the ISM is lost altogether in the formation of light stars ($<0.8 M_{\odot}$) which never return material to the ISM.

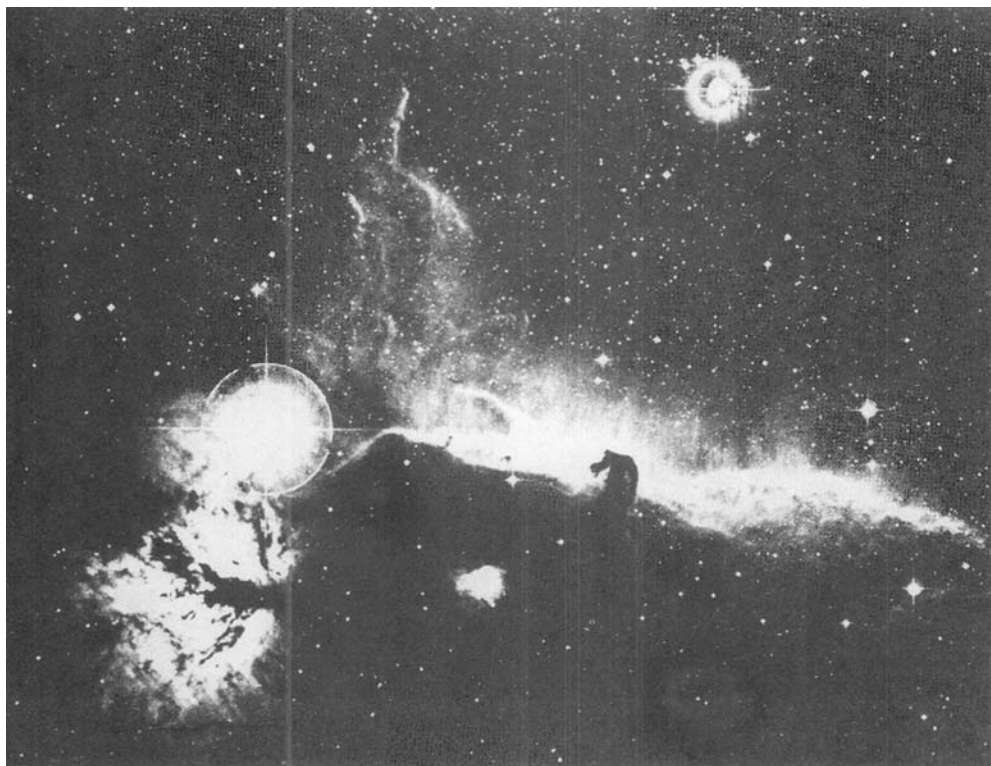


FIG. 2. The bright emission nebula IC434 silhouetting the Horsehead dark cloud in Orion (taken from Murdin, Allen and Malin 1979 UKSTU). Compare this picture with the map in Fig. 26. NGC2024 lies just to the NE of ζ Orionis the easternmost star in the belt of Orion. IC434 glows due to photoionization by σ Orionis which though less bright and more distant than ζ Orionis it is a more efficient ultraviolet emitter. (Note: North is left and East is down).

The stars which form from the ISM emit radiation and ionize the gas around them causing these clouds to glow visibly. These are the bright emission nebulae (Fig. 2) which emit the spectra of atomic H due to the radiative decay of excited H atomic states produced by proton-electron recombination. This recombination radiation gives rise to the beautiful colour photographs of nebulae, such as the Orion nebula M42, which are to be found in all books on astronomy. The size of the glowing so-called HII region depends critically on the type of star. The sun is a rather feeble star compared with those in the Trapezium cluster which powers the Orion nebula and causes a volume of the order of 1 ly in diameter (approximately 10^9 times the volume encompassing the solar system) to glow quite brightly. There is a less brightly glowing halo around the Orion nebula which is much larger—roughly 10 ly.

Often associated with these bright nebulae are clouds of dark obscuring material (Fig. 2) whose scattering properties have been studied for some time and which are thought to contain interstellar grains or dust. These are deduced to be micron or submicron sized particles from the wavelength dependence and polarization properties of the scattered radiation (Dyson and Williams, 1980).

These dark clouds were originally thought to be holes in the celestial sphere through which one could peer deep into space and it has only recently become appreciated that

these objects are quite black and essentially impenetrable by short wavelength radiation. As a consequence the grains are able to protect any molecules inside the clouds from dissociation by the starlight which pervades much of the rest of space and originally thought to pervade *all* space.

These clouds vary in almost all parameters such as: opacity, size, shape, density, temperature, internal turbulence, overall velocity, temperature homogeneity, proximity to stars and emission nebulae, apparent elemental composition, ratio of ions/electrons/molecules/radicals, whether hot or cool stars or protostars are in the vicinity or embedded, etc.

As a result there are numerous possible classifications and sub-classifications of the clouds, in fact each reviewer can have his own. For the purposes of this review it is convenient to point out that molecules are found in the following regions

1. Diffuse clouds
2. Dark clouds
3. Circumstellar shells
4. Stellar atmospheres
5. Comets

as well as of course planets (in the solar system).

As well as these regions there are interarm regions with $n \sim 10^{-1} \text{ cm}^{-3}$ and also an intergalactic medium with $n \sim 10^{-4} \text{ cm}^{-3}$ and two possible effective temperatures due to the radiation field, 10^4 or 10^6 K.

Turner (1979a) has presented a general survey and classification of the regions where interstellar molecules reside. The most important point as far as interstellar chemistry is concerned is cloud opacity. If a cloud is transparent i.e. a diffuse cloud, then molecular lifetimes are limited by photodissociation by the ultraviolet radiation from stars. Such clouds have $T \sim 80$ K, mass $\sim 4 \times 10^2 M_{\odot}$, size ~ 15 ly and number density (H atoms + H_2 molecules) $n \sim 0.1 \text{ cm}^{-3}$. If on the other hand the cloud is opaque to starlight any molecules formed may be very long-lived indeed. For the dark clouds $T \sim 10$ K, mass $\sim 10\text{--}100 M_{\odot}$, size $\sim 1\text{--}3$ ly and $n \sim 1\text{--}10 \text{ cm}^{-3}$ (mainly H_2). There are larger inhomogeneous clouds often associated with stars and sometimes called molecular clouds where $T \sim 25\text{--}50$ K and $n \sim 10^4\text{--}10^5 \text{ cm}^{-3}$ in their cores and $T \sim 10$ K and $n \sim 10^3 \text{ cm}^{-3}$ in the less dense outer regions. The masses involved are $\sim 10^4 M_{\odot}$ and sizes range from 3–100 ly. The largest clouds of all are the giant molecular clouds (GMCs) which may have masses $\sim 10^5\text{--}2.5 \times 10^6 M_{\odot}$ and sizes 100–500 ly. The most recent studies are yielding information about much denser and much hotter regions.

SPECTROSCOPY

Introduction

Quantum mechanics in so far as it applies to spectroscopy can be classified into two problems.

1. The time independent problem, relates to the energy level manifold of the atom or molecule and generates the eigenvalues $E(n)$ and associated eigenstates, $|n\rangle$.
2. The time dependent problem, considers the conditions under which an interstate transition $|n\rangle \rightarrow |m\rangle$ can take place either spontaneously or under the influence of a perturbation by radiation or a collision with another molecule or atom.

In the case of molecules the treatment of the first problem almost inevitably starts with the Born-Oppenheimer separation (Born and Huang 1954) which allows the electronic, vibrational and rotational motions to be treated separately and the associated state manifolds to be evaluated independently and then combined. For a finer understanding and indeed for a true insight into the problem one in general then juggles the basic results using a perturbation approach to allow for intermotional effects which are, in our case, mainly vibration-rotation interactions. These are in general small, but interesting, and under high resolution often very important. Into this basic treatment one may often have to inject further, initially disregarded, effects which relate to the specific molecule. The most important interactions that may in certain cases need to be considered are:

1. Internal rotation splitting
2. Conformational isomerism
3. Quadrupole hyperfine interactions
4. Electron spin interactions (for free radicals)

There are others which are *usually* less important. However one should note that in the Universe, anything that one can conceive might happen, undoubtedly does—and then some.

This field has benefitted as much, if not more so than most others, from the ingenuity with which scientists have unravelled the atomic and molecular Hamiltonians. The diverse problems associated with interstellar spectroscopy will be dealt with in the section which deals with the observational data.

As the results of the time dependent problem apply to all the systems in general they can be summarized first and they can usually be put under the heading—the interaction of radiation with matter. In fact, it was this general problem which gave birth to quantum mechanics (Van der Waerden, 1967).

The most important result of the time-dependent analysis of the radiation/molecule interaction lies in the quantitative evaluation of the resonant absorption coefficient $\gamma(\omega)$ in the Beer-Lambert law

$$I(\omega) = I_0(\omega)e^{-\gamma(\omega)l} \quad (1)$$

$I(\omega)$ and $I_0(\omega)$ are transmitted and incident radiation intensities and l the length of the absorbing medium, here assumed homogeneous. The Fermi golden rule (Fermi, 1961) yields the general result

$$\gamma(\omega) = \frac{8\pi^3}{3hc} \omega(N_m - N_n) |\langle n|\mu|m \rangle|^2 S(\omega, \omega_0) \quad (2)$$

(Kroto, 1975) where ω is the frequency, N_m and N_n are the populations* of the connected states, $\langle n|\mu|m \rangle$ is the electric dipole moment matrix element and $S(\omega, \omega_0)$ is a normalized line shape function. From this relation we see that $\gamma(\omega)$ is proportional to ω and thus the higher the frequency the stronger the interaction. Thus microwave transitions at 30 GHz ($\equiv 1 \text{ cm}^{-1}$) are inherently 20 000 times weaker than optical transitions at 5000 Å ($\equiv 20\,000 \text{ cm}^{-1}$). $S(\omega, \omega_0)$ in the case of laboratory microwave studies is usually a Lorentzian peaking sharply at the centre frequency ω_0 (Townes and Schawlow, 1955) and associated with pressure broadening.

The population factor $N_m - N_n$ determines the nature of the spectrum quite critically. There are three main cases.

* Note if the states have degeneracies g_m and g_n then $(N_m - N_n)$ must be replaced by $(N_m/g_m - N_n/g_n)$.

1. $N_m > N_n$ and $I(\omega) < I_0(\omega)$: in this case $\gamma(\omega)$ is positive and (stimulated) absorption occurs. This is usually the case in the laboratory where roughly equilibrium conditions (for which $N_m = N_n e^{-\Delta E/kT}$) are usually maintained.
2. $N_m = N_n$ and $I(\omega) = I_0(\omega)$. This is the case of saturation and the active volume is effectively transparent.
3. $N_m < N_n$ and $I(\omega) > I_0(\omega)$. In this case we have so-called population inversion, more radiation is emitted than is incident and we have effectively maser or laser amplification.

Selection rules

The selection rules which govern the transitions follow directly from the *electric dipole* matrix element $\langle n | \mu | m \rangle$. In general the most important ones for our purpose are

$\Delta J = 0, \pm 1$, for rotational transitions

$\Delta v = \pm 1$, for vibrational energy changes

$S \leftrightarrow T$, singlet-triplet electronic transitions are forbidden.

There are however many loopholes through which the molecule can pass and as we may be dealing with effects over millions of years one must note that even very strongly forbidden processes may take place given enough time (1000 million years!) A more complete study of radiation/molecule interactions indicates that:

1. *Electric dipole* transitions are the strongest.
2. *Magnetic dipole* matrix elements are smaller by the factor $\alpha = 1/137$ (the fine structure constant) and so magnetic interactions are $\alpha^2 (\sim 0.5 \times 10^{-4})$ weaker than the electric interaction.
3. *Electric quadrupole* transitions are weaker by the factor $(a/\lambda)^2$ where a is a molecular dimension and λ is the radiation wavelength (Mott and Sneddon, 1963). For optical electronic transitions these are weaker, by $\sim 10^{-8}$, than electric dipole interactions.
4. There are numerous other processes which can, in the absence of other stronger effects, become important. In this class come weak second-order effects such as Rayleigh, Raman and higher order scattering processes.
5. Finally we should note that some other important processes must be taken into account:
 - (a) Photoionization
 - (b) Photodissociation
 - (c) Collisions

The most important recent breakthroughs in this field have come via the marriage of molecular microwave spectroscopy and radio astronomy. The most important aspects of microwave spectroscopy are therefore dealt with in more detail in this section than those of infrared and electronic spectroscopy which are in any case rather more familiar. The latter techniques have however very recently made exciting contributions and undoubtedly will play even more significant rôles in the future and so any relevant points are also highlighted in context with observation.

Spectroscopy is a subject for which many books have been written and almost all aspects have been well covered. More aspects of microwave spectroscopy have been covered by Townes and Schawlow (1955), Wollrab (1967), Gordy and Cook (1970) and Kroto (1975). The books by Herzberg (1944, 1945, 1950, 1966) have covered most aspects of electronic and molecular vibrational spectroscopy.

Microwave spectroscopy

There are several factors which have combined to make microwave spectroscopy a most effective analytical technique. The first is the very high resolution which, together with the high degree of pattern specificity, allows such moderately complex molecules as ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), glycine ($\text{NH}_2\text{CH}_2\text{COOH}$) and vinyl cyanide ($\text{CH}_2=\text{CHCN}$) to be unequivocally identified in extremely complex mixtures. Lines at approximately 30 000 MHz ($\equiv 1 \text{ cm}^{-1}$) can be measured routinely to 100 kHz and with specialized techniques to a few kHz if necessary. The interstellar cell in which more than 50 molecules have been detected still yields isolated lines rather than dense long grass though this may change as sensitivity improves.

Another obvious reason is that the atmosphere is relatively transparent to radio waves. Finally we should note that at low temperatures only low frequency transitions are excited to *emit* and so there is no infrared or electronic emission from the cold clouds. These latter techniques would require background radiation to be transmitted through the clouds and allow *absorption* to be detected.

The first microwave experiments were carried out by Cleeton and Williams (1934) at the behest of Dennison who was interested in measuring the ammonia (NH_3) tunneling frequency directly. Cleeton and Williams constructed a 24 GHz valve oscillator and used a leather bag as an absorption cell. The war saw the development of klystron oscillators and more sophisticated cells made from wave guide. Most molecular microwave measurements have been made using the Hughes-Wilson (1947) Stark modulation design which has culminated in the quintessential Hewlett Packard 8460A spectrometer now, regrettably, no longer available.

There are a few general points of which it is important to be aware.

1. Light diatomic and triatomic molecules such as CO and HCN tend to have their most intense transitions at approximately 100 GHz or higher frequencies and so are studied by millimetre or more readily by far infrared techniques (Dowling, 1967).
2. Most other molecules which have at least three heavy atoms (mass 12 amu or more) tend to have accessible rotational transitions in the 8–40 GHz microwave range ($\equiv 0.27\text{--}1.3 \text{ cm}^{-1}$).
3. If a molecule is very heavy and complicated its spectrum may consist of so many lines that no individual line may be sufficiently strong to be detectable.
4. Often a molecule may not be sufficiently volatile as pressures of 1–100 $\mu\text{m Hg}$ are usually necessary. Raising the temperature may destroy the compound or may populate more states causing line dilution, as in case 3.
5. As far as free radicals and ions are concerned, their microwave spectra are very difficult to detect compared with the success of electronic spectroscopy—mainly due to the very much higher absorption coefficients and superb sensitivity and integrating capabilities of the simple photographic plate.
6. Numerous ingenious techniques have been, and are being, developed to circumvent these problems and astronomy has given the field a shot in the arm.
7. A rather important factor tends to make the spectra of linear molecules more readily detectable than those of non-linear molecules. The linear molecule has only two rotational degrees of freedom and as a consequence that is only *one* line for a given $J + 1 \leftrightarrow J$ transition, whereas for the non-linear species this will in general be a multiplet. In the case of a symmetric rotor it would have $J + 1$ components (see next section) and in the asymmetric rotor case in general even more.

Rotational energy levels

The Hamiltonian for a rigid rotating molecule can be written (Kroto, 1975)

$$H_r = AJ_A^2 + BJ_B^2 + CJ_C^2 \quad (3)$$

where J_A , J_B and J_C are components of angular momentum (units of \hbar) along the molecule-fixed principal axes. A , B and C are rotational constants which are related to the principal moments of inertia I_A , I_B and I_C by $A = 1/2I_A \dots$ etc.* By convention $I_A \leq I_B \leq I_C$ and therefore $A \geq B \geq C$. The solution of H_r depends on the type of molecule. Thus for linear molecules such as CO, OCS and $\text{HC}\equiv\text{C}-\text{C}\equiv\text{N}$ where $B=C$ and $J_A \rightarrow 0$ the resulting energy is given by the familiar expression

$$E(J) = BJ(J+1) \quad (4)$$

where J is the overall angular momentum quantum number.

Symmetric tops such as $\text{CH}_3\text{C}\equiv\text{N}$, $\text{CH}_3(\text{C}\equiv\text{C})_3\text{H}$ and SF_5Cl , which are prolate (i.e. cigar shaped) with $A > B = C$, can spin about their symmetry axes, with associated quantum number K , and the energy is given by

$$E(J, K) = BJ(J+1) + (A-B)K^2 \quad (5)$$

A similar expression in which $A \rightarrow C$ applies to oblate tops such as NH_3 and C_6H_6 which are disc shaped.

Spherical tops, such as CH_4 and SF_6 , have $A = B = C$ and the energies follow a similar expression to that for linear molecules.

Asymmetric top molecules have $A > B > C$ and their energy levels follow much more complicated expressions. It is however very informative to consider a molecule which is not too asymmetric. Consider a *near* prolate molecule in which $A > B \sim C$. In this case the energy, using perturbation theory, is given by

$$E(J, K_A) = \bar{B}J(J+1) + (A-\bar{B})K_A^2 \pm \frac{1}{4}\delta_{K_A,1}(B-C)J(J+1) \dots \quad (6)$$

where $\bar{B} = \frac{1}{2}(B+C)$ and K_A is a *good enough* quantum number \equiv to $|K|$ (which for a symmetric top is *almost* perfect). The last term has a Kronecker delta which indicates that it splits the degeneracy of the $|K| = 1$ levels only. Smaller terms, which shift and/or split other levels, come in only in second order and have been truncated.

If a molecule is very asymmetric the energy level pattern can become very complicated as can the resulting spectrum. A comparison of the energy level patterns for the three cases is given in Fig. 3. For the asymmetric molecule it is necessary to further specify the levels because as can be seen in Fig. 3c levels of a given $|K|$ (or here K_A) are no longer degenerate. It is usual to use the value of $|K|$ with which the level correlates in the oblate limit (K_C). Thus a given level is characterized by $J_{K_A K_C}$.

Rotational spectra

For a linear molecule with a dipole moment $\Delta J = \pm 1$ and the transitions are governed by the expression

* $I_A = \sum_n m_n(r_B^2 + r_C^2)$, $I_B = \dots$ etc. where m_n are the atomic masses and r_A , etc. are the coordinates $A(\text{MHz}) = 505391/I_A(\text{amu}\text{ \AA}^2)$ or $A(\text{cm}^{-1}) = 16.858/I_A(\text{amu}\text{ \AA}^2)$.

Example. For CH_3CN or $\text{CH}_3(\text{C}\equiv\text{C})_n\text{H}$, $\angle\text{CCH}$ and $r(\text{CH})$ are respectively tetrahedral and ~ 1.1 \AA long. Thus the distance from the A axis is ~ 1.04 \AA $\therefore I_A = 3(1.04)^2 \sim 3.23$ amu \AA² $\therefore A \sim 5.2$ cm⁻¹ or 156.5 GHz.

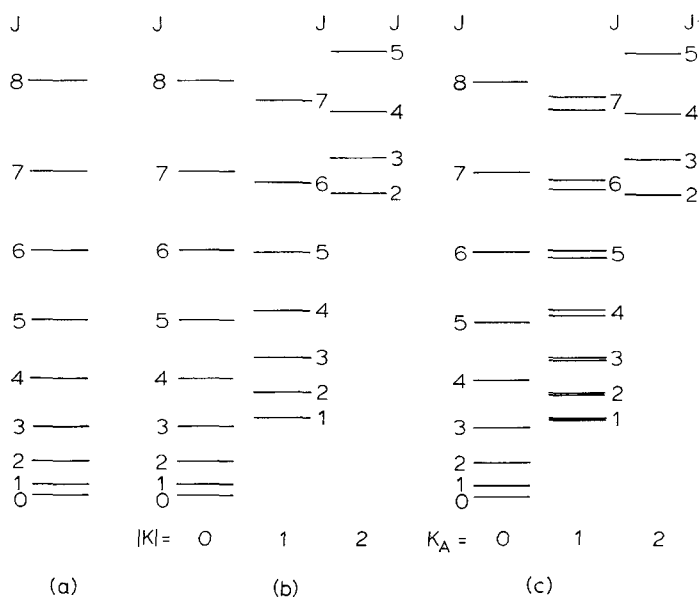


FIG. 3. (a) The rotational energy levels of a linear molecule. (b) The rotational energy levels of a prolate symmetric top. (c) The rotational energy levels of a prolate slightly asymmetric rotor. For this set of diagrams $A \sim 38$ GHz, $B \sim C \sim 30.6$ GHz and $B - C \sim 0.25$ GHz. In all three cases vertical transitions may occur depending on the dipole moment conditions. In such cases the transitions give rise to equidistantly spaced lines for a linear molecule and equidistantly spaced groups of lines in the non-linear cases.

$$\Delta E(J) = 2B(J + 1) \quad (7)$$

This gives rise to a sequence of equally spaced lines (separation = $2B$) and the textbook example obtained by Dowling (1967) in the far infrared is shown in Fig. 4. The microwave spectrum of $\text{HC}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$ which also shows strong vibrational satellites is shown in Fig. 5.

The selection rules that apply to rigid symmetric tops are $\Delta J = \pm 1$ and $\Delta K = 0$. The selection rule on K essentially means that the radiation field cannot exert a torque about the symmetry axis, as there is no perpendicular dipole component, and cannot therefore make it spin any faster or slower about this axis. Consequently only vertical transitions in

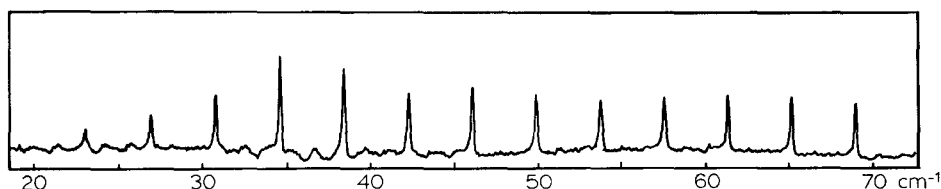


FIG. 4. Part of the far infrared pure rotational spectrum of CO obtained by Dowling (1967). The background intensity varies across the range and so distorts the apparent intensity distribution. The lines are separated by $2B_0$ which can be obtained directly from this spectrum and once this has been determined it is straightforward using eq. (7) to assign the J numbers of the lines.

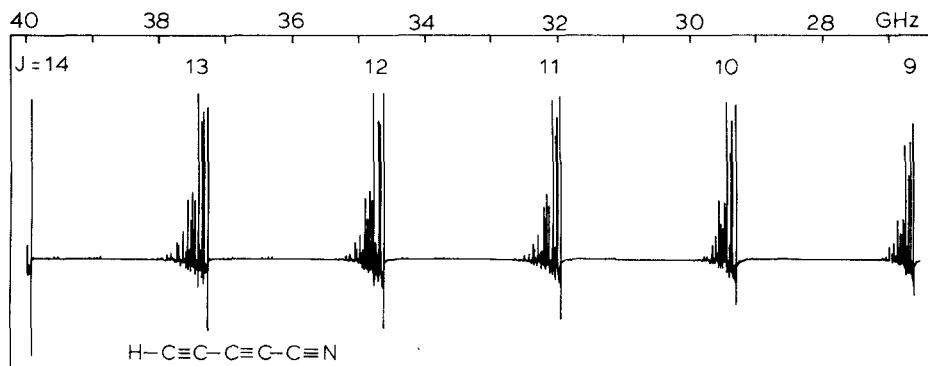


FIG. 5. The laboratory microwave rotational spectrum of cyanobutadiyne, $\text{HC}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$ (Alexander, Kroto and Walton, 1976). Instead of a single line, each $J + 1 \leftarrow J$ ground state line is accompanied, to high frequency, by a complicated entourage of bending vibration satellites. The first line at the RH end of each group is the ground state line. The very weak features which lie to the low frequency side are transitions belonging to the ^{13}C and ^{15}N monosubstituted species. Note that the microwave spectra have negative-going Stark lobes as with this Stark spectrometer the zero field spectrum is presented positively and the field split spectrum negatively.

the $|K|$ manifolds of Fig. 3b may occur, giving rise to a spectrum governed by the same expression as for a linear molecule, Eq. (7). Such a spectrum in the microwave range is shown in Fig. 6 for $\text{CH}_3(\text{C}\equiv\text{C})_2\text{C}\equiv\text{N}$. A nice example of a far infrared spectrum is given by Ozier, Ho and Birnbaum (1969) for CH_3D . There is an added complication in that vibrational satellites are also detected in microwave spectra as discussed in the next section. The various $|K|$ components for a given value of $J + 1 \leftarrow J$ overlap if centrifugal distortion (next section) is negligible as is the case in the low resolution run shown in Fig. 6. Although a spherical top has no permanent dipole moment it distorts on rotation and gives rise to a distortion-induced rotational spectrum (Watson, 1971, Rosenberg, Ozier and Kudian, 1972).

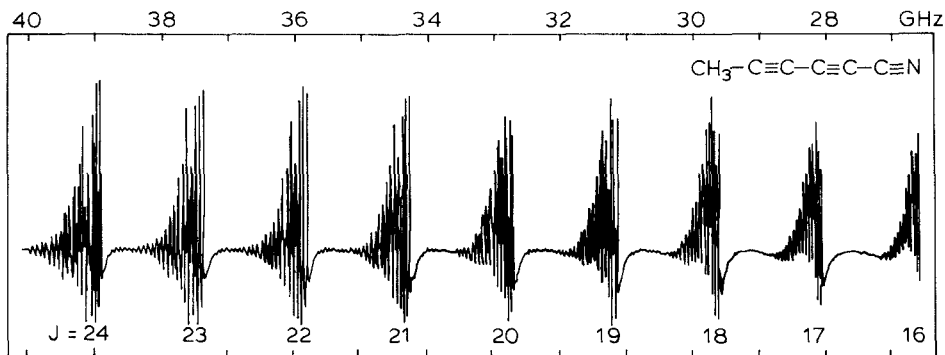


FIG. 6. Wide band scan of the microwave spectrum of $\text{CH}_3\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$ (Alexander *et al.*, 1978). As in the case of cyanobutadiyne the first line at the RH end of each group belongs to the vibrational ground state and the rest to bending vibrational satellites. The ground state transitions can be resolved into $|K|$ multiplets under higher resolution (Fig. 10).

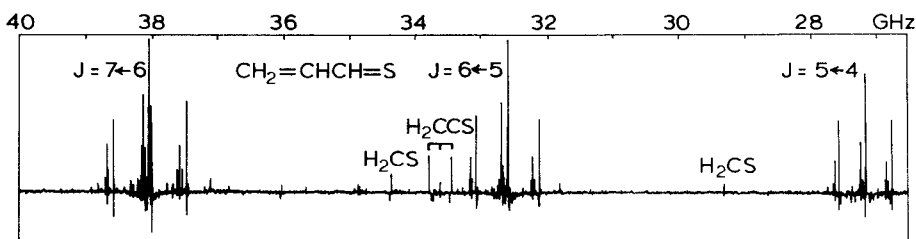


FIG. 7. The microwave spectrum of *trans*-2-propenethial $\text{CH}_2=\text{CHCH}=\text{S}$ produced by pyrolysis of diallylsulphide (Georgiou and Kroto, 1980). The most prominent features are the three groups of R-branch transitions which display the characteristic pattern of a slightly asymmetric rotor. The $K_A = 1$ lines flank the central ($K_A \neq 1$) group roughly symmetrically. Lines of H_2CS and H_2CCS are also observed.

Asymmetric rotor molecules may have very complex spectra. However the most frequently observed transitions often occur for near prolate molecules with a dipole component μ_A along the long A axis. Accordingly we will deal only with the spectra for this special and most important case in detail. The most important effect of asymmetry as we have noted is the splitting of the $K_A = 1$ levels (Fig. 3c). The *main* μ_A selection rules are analogous to those for a symmetric rotor i.e. $\Delta J = \pm 1$ and $\Delta K_A = 0$ and thus an analogous type of spectrum occurs. Transitions occur from upper to upper and lower to lower $K_A = 1$ split levels and so the transition energy relation from Eq. (6) is

$$\Delta E = 2\bar{B}(J+1) \pm \frac{1}{2}\delta_{K_A,1}(B-C)(J+1) \quad (8)$$

This splits the $K_A = 1$ lines out as two single lines which symmetrically flank the central bunch for a given J . This effect is shown under low resolution in Fig. 7 for $\text{CH}_2=\text{CHCH}=\text{S}$. These are called μ_A R-branch lines because they have $\Delta J = +1$ and are associated with the μ_A dipole moment. An asymmetric rotor may have other non-zero dipole moment components and these will generate other types of transitions. For instance a dipole moment perpendicular to μ_A , either μ_B or μ_C , will allow the molecule to be twisted about by its long axis by the radiation and this allows K_A to change by $\Delta K_A = \pm 1$. The splitting is the quantum effect equivalent to classical wobbling which occurs for an object which is not a good top. Under high resolution, as is shown in Fig. 8, we see the effect in detail. In fact we can also see that second order effects of asymmetry also split $K_A = 2$ lines. The splitting is much smaller for, as one expects, wobbling gets less important as the molecule spins more rapidly about the axis i.e. as K_A increases relative to J .

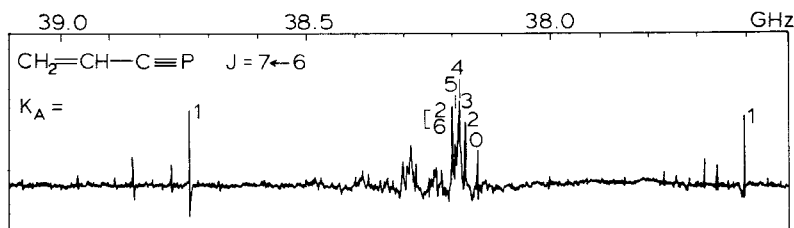


FIG. 8. A moderate resolution microwave scan of the $J = 7 \leftarrow 6$ transition of $\text{CH}_2=\text{CHC}\equiv\text{P}$ the phosphorus analogue of $\text{CH}_2=\text{CHC}\equiv\text{N}$, vinyl cyanide. The vibrational ground state lines have been labelled by the value of K_A (Ohno, Kroto and Nixon, 1981).

An important transition, called a K -doubling transition, can occur *between* the $K_A = 1$ split levels. From Eq. (6) we see that the transition energy is given by

$$\Delta E = \frac{1}{2}(B - C)J(J + 1) \quad (9)$$

Spin statistics

In a molecule such as H_2CO with two identical H atoms the rotational states with odd and even values of K_A have different spin statistics. The situation is similar in the rotational

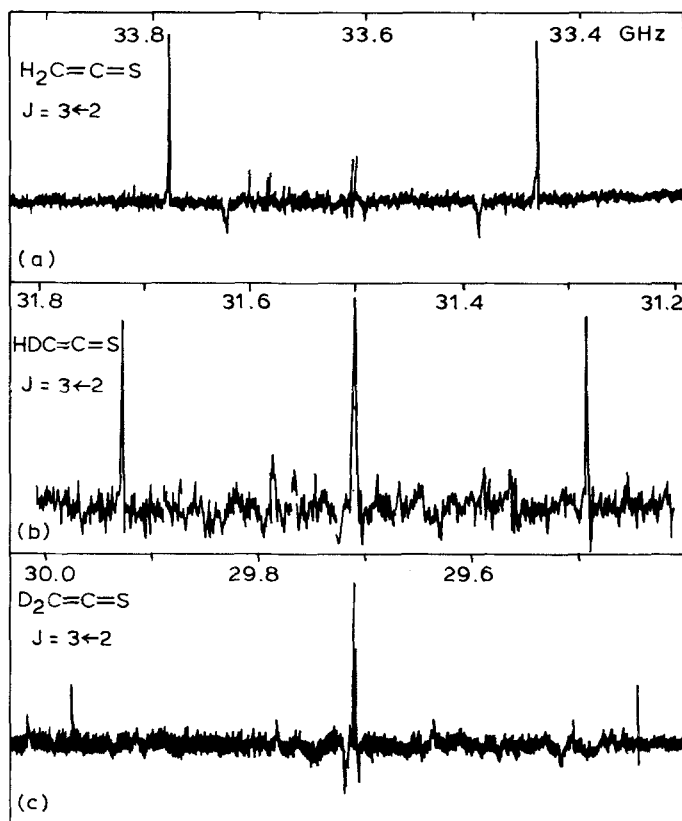


FIG. 9. The microwave spectra of $J = 3 \leftarrow 2$ transitions of the thioketenes $\text{H}_2\text{C}=\text{C}=\text{S}$, $\text{HDC}=\text{C}=\text{S}$ and $\text{D}_2\text{C}=\text{C}=\text{S}$ (Georgiou, Kroto and Landsberg, 1979). These are slightly asymmetric rotors with central lines having $K_A = 0, 2$ and outer lines $K_A = 1$. In H_2CCS and D_2CCS rotation about the axis exchanges equivalent nuclei and so the generalised Pauli Exclusion Principle controls the statistical weights of states with odd and even K_A . A similar effect occurs for H_2 where it explains the *ortho-para* ratio (Kroto, 1975). For H_2CCS the *ortho* states with statistical weight 3 have K_A odd and *para* states with statistical weight 1 have K_A even. Thus the outer lines are $3 \times$ as intense as the central lines. The D nuclei are bosons so the statistics reverse and yield *ortho:para* (K_A even: K_A odd) 2:1. In HDCCS the statistics do not apply and the intensities are normal. Note that transitions do not occur between the *ortho* and *para* manifolds and so one can essentially think of them as two different molecules.

states of H_2 for which ortho H_2 may only have odd J and para H_2 even J . For molecules like H_2CO , H_2CCO and H_2CCS , levels with K_A odd have three times the statistical weight of levels with K_A even, a factor reflected directly in the intensities of associated transitions. For D_2CCS this changes to 2 to 1 for K_A even and K_A odd because D nuclei are bosons and in HDCCS permutation statistics do not apply. This is a nice example of the generalized Pauli Exclusion principle (Kroto, 1975) and the experimental effect is shown in Fig. 9. This effect is also important in symmetric tops as indicated below. One can consider the two sets of levels as effectively different molecules between which transitions do not occur.

Centrifugal distortion

Centrifugal effects which tend to increase the molecular dimensions with increasing J are usually quite adequately taken into account by J^4 corrections introduced using perturbation theory. For a linear molecule the centrifugal distortion correction to the

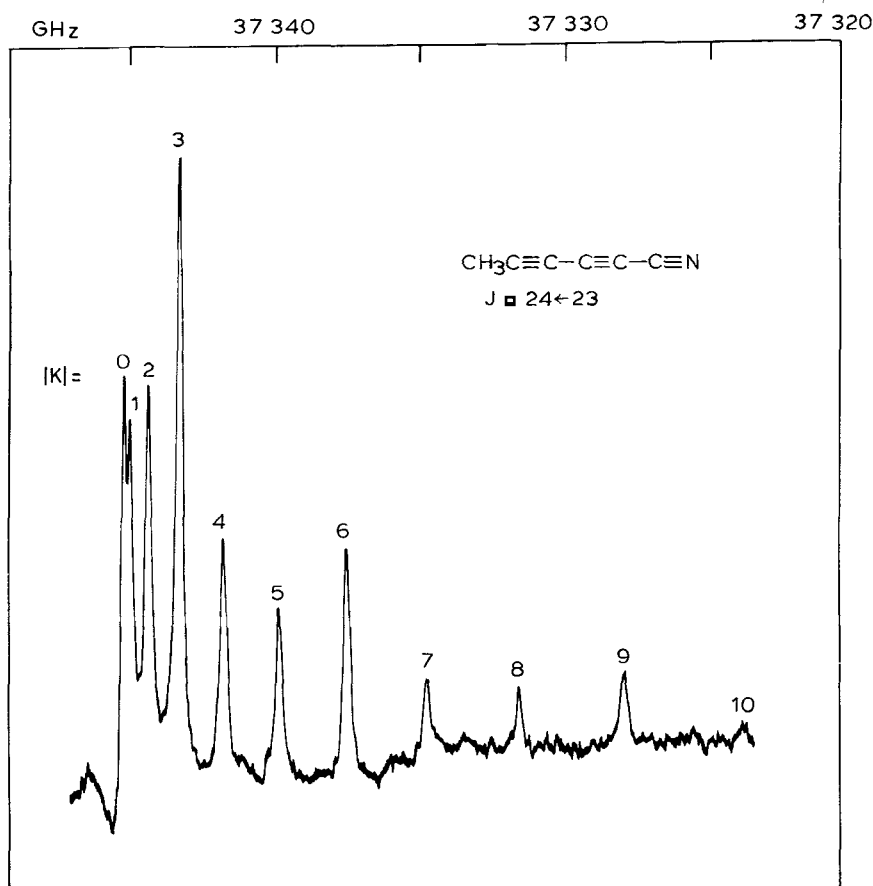


FIG. 10. Part of the $|K|$ structure of the $J = 24 \leftarrow 23$ transition of $CH_3C\equiv C-C\equiv C-C\equiv N$ (Alexander *et al.*, 1978). The higher $|K|$ levels are not sufficiently populated to be detected at this temperature (~ -60 K). Note that statistical weights of levels with $|K|$ a multiple of 3 are twice those for the rest.

energy (Eq. (4)) is $-DJ^2(J+1)^2$ where $D \sim 10^{-6} B$ (for a diatomic molecule $D = 4B^3/\omega^2$ where ω is the vibrational frequency). The resulting transition expression is

$$E(J) = 2B(J+1) - 4D(J+1)^3 \quad (10)$$

For the symmetric top, the correction which must be added involves three centrifugal distortion terms $-D_J J^2(J+1)^2 - D_{JK} J(J+1)K^2 - D_K K^4$ (Slawsky and Dennison, 1939; Kroto 1975) which results in transitions governed by the expression

$$\Delta E(J, K) = 2B(J+1) - 4D_J(J+1)^3 - 2D_{JK}(J+1)K^2 \quad (11)$$

As a consequence a given $J+1 \leftarrow J$ symmetric top transition is split by the small D_{JK} term into a sequence of close quadratically spaced $|K|$ components as is shown in Fig. 10 for $\text{CH}_3(\text{C}\equiv\text{C})_2\text{C}\equiv\text{N}$. Note here how spin considerations cause transitions with $|K|$ a multiple of 3 to have twice the statistical weight of the others (Kroto, 1975).

More complex centrifugal corrections apply for the general asymmetric rotor (Watson, 1967) which as far as qualitative patterns are concerned are in general masked by the larger shifts and splittings due to asymmetry.

Ground and vibrationally excited states

Many molecules have vibrational frequencies sufficiently low that their laboratory spectra show rotational transitions of vibrationally excited states. Bending vibrations associated with low force constants, and therefore low frequencies, are often observed. They tend, in the case of linear chains, to yield shorter effective bond lengths, the moments of inertia tend to decrease and the rotational constants to increase. Good examples of this are shown in Figs. 5 and 6 where long sequences of vibrational satellites are shown. In a linear molecule such as $\text{N}\equiv\text{C}-\text{C}\equiv\text{P}$ shown in Fig. 11 we see that the $v=1$ level is split into a doublet by an effect which can be related to the $K_A=1$, splitting in asymmetric rotors (Watson, 1965). This effect, known as l -doubling (Herzberg, 1945, Nielsen, 1950), occurs in all cases where the bending vibration quantum number v is odd. In general the effect is treated as a vibration-rotation coriolis interaction (Nielsen, 1950).

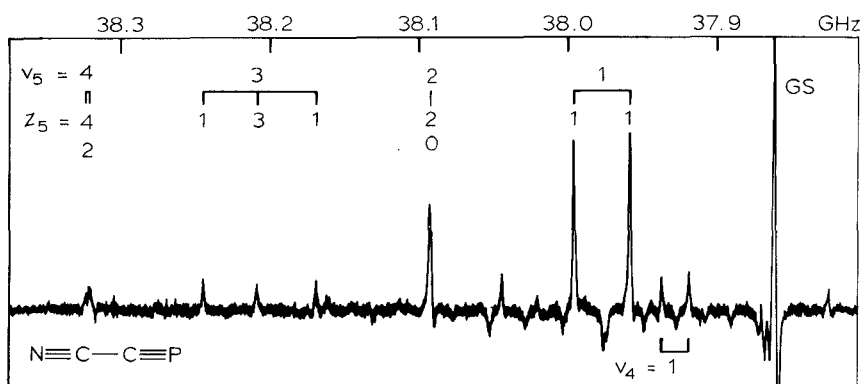


FIG. 11. The microwave spectrum of the $J = 7 \leftarrow 6$ transition of $\text{N}\equiv\text{C}-\text{C}\equiv\text{P}$ (Cooper *et al.*, 1979). The spectrum is very similar to that of $\text{HC}\equiv\text{C}-\text{C}\equiv\text{N}$. The vibrational satellite pattern is characteristic of a simple linear molecule with a low bending frequency. The $v=1$ satellite consists of two lines split apart by l -doubling, a vibration-rotation counterpart of asymmetry K -doubling and electron-rotational Λ -doubling.

The rotational constants are usually identified by the appropriate vibrational quantum number subscripts and for the ground state in particular they are written A_0 , B_0 and C_0 associated with I_A^0 , I_B^0 and I_C^0 respectively.

Conformers and internal rotation effects

Some molecules have rotational isomers. For instance the molecule isocyanatoethene $\text{CH}_2=\text{CHNCO}$ with an angle of about 140 degrees at N has two conformers, *cis* and *trans* species (Bouchy and Roussy, 1978; Kirby and Kroto, 1978). The moments of inertia of the two isomers are quite different as are the dipole moments and hence the rotational spectra (Fig. 12) are also quite different and it is important to note that although the *cis* spectrum is clearly very weak this isomer is present in approximately 35 per cent proportion.

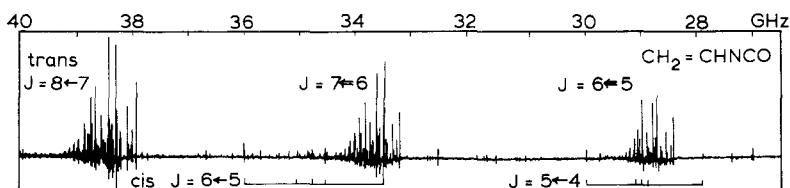


FIG. 12. The microwave spectrum of $\text{CH}_2=\text{CHNCO}$ (Kirby and Kroto, 1978). The strong groups of lines belong almost entirely to *trans* $\text{CH}_2=\text{CHNCO}$ ($\angle\text{CNO} \sim 140$ degrees). Some very weak features, the strongest of which are assigned below the baseline, belong to the *cis* conformer. Though the *cis* species is present in ~ 35 per cent abundance the lines are very much weaker due to greater asymmetry and lower dipole moment.

The barrier between rotational conformers in some cases is sufficiently low that appreciable tunnelling occurs during the timescale of the experiment. This can cause internal rotation splittings to be observable.

Other types of isomerism can occur such as in the case of cyanides and isocyanides. The rotational spectra of both CH_3CN and CH_3NC were well known but, as discussed later, the interstellar spectrum of HNC was detected before the laboratory measurement was made.

Quadrupole splittings

Nuclei with spin $I \geq 1$ possess non-spherical charge distributions and therefore quadrupole moments which can interact with electric field gradients of molecular charge distributions. This causes hyperfine splittings which are largest for low J and high K . The splitting pattern depends qualitatively on I and quantitatively on the nucleus in question and its bond location. These hyperfine patterns have been very valuable in interstellar identifications as shown later. The splittings tend to decrease roughly as J^{-3} so in general only low J lines show these splittings. For linear molecules with N atoms, for which the quadrupole parameters are only a few MHz or less, only the lowest J lines with $J \sim 0-2$ show resolvable structure in general. In symmetric tops the highest $|K|$ lines, for a given J , show splittings.

Dipole moments

The most accurate dipole moments are in general obtained by studying the Stark effect in rotational spectra. These values are particularly important in molecular radio astronomy

as the line intensities are so dependent on their values through the relation for the absorption coefficient $\gamma(\omega)$ in Eq. (2). Many values are listed by Gordy and Cook (1970).

Free radicals

Some molecules have unpaired electrons which give rise to electronic angular momenta that interact in complicated ways with the rotational motion. The energy level patterns produced depend quite critically on the molecule in question. Suffice it to say that further splittings can, and often do, occur. In fact the first molecule detected, OH, was detected by a transition which occurs *between* two levels split apart by a Λ -doubling interaction, an interaction and therefore a type of transition which does not occur in diamagnetic molecules. The radio spectrum of CH has also been detected by this type of transition. The hyperfine splittings that can arise in these systems have, as we shall see, been very important in the identification of some unexpected and exciting species. The Λ -doubling splitting arises by a type of coriolis splitting of the electronic angular momentum about the bond axis caused by interaction with overall rotation (Townes and Schawlow, 1955; Carrington, 1974; Kroto, 1975).

Most free radicals have been detected by electronic spectroscopy and their electronic properties are discussed by Herzberg (1950, 1966). Some have also been detected by gas-phase paramagnetic resonance as discussed by Carrington (1974). Laser magnetic resonance is proving to be one of the most powerful and sensitive techniques for studying these species (Evenson *et al.*, 1979) and much effort is also being applied to detect their zero field microwave spectra.

Electronic and vibrational spectra

The first interstellar molecules were indeed diatomic molecules detected by their electronic spectra. The main characteristics of these spectra are rather more familiar to the non-specialist than are those of microwave spectra and so a detailed introduction is not given in this review. Important features will however be discussed in context with the astrophysical results. A complete discussion covering most major aspects of electronic as well as vibrational and rotational spectra of diatomic molecules has been given by Herzberg (1950). So far no interstellar polyatomic molecules have been detected by their electronic spectra though the species C_3 and H_2O^+ have been detected in comets. Their electronic spectra have been discussed in detail by Herzberg (1966).

The problems involved in detecting vibrational spectra are only just being solved and the first results are very exciting. The vibrational spectra of polyatomic molecules have also been discussed by Herzberg (1945) and, in this review, will also only be discussed very briefly in context with observations. It is possible that infrared spectroscopy will yield as much data in the future as radio spectroscopy is doing at present.

Astronomical observation

The main information which can be derived from molecular spectra, apart of course from the molecular identity, relates to the abundance and the physical conditions that pertain in the molecular clouds. This information is buried in the transition intensities, the line shapes and the observed line frequencies. There are three main problems that tend to confuse the issue: namely temperature, number density and cloud velocity.

Temperature. Temperature is really only a well defined quantity when equilibrium conditions apply and the distribution of the molecules among the energy levels obeys the Boltzmann relation. This is not in general the case in the ISM and the distributions are governed by a subtle interplay of collisional and radiative processes. It is convenient to describe any individual two level distribution N_n/N_m by an effective (Boltzmannian) temperature and call this the excitation temperature T_{ex} . In the case of the molecular radio lines this will in general be the rotational excitation temperature and it may often vary from one pair of rotational levels to another. In a similarly parochial and suspect manner one can define a kinetic temperature T_k which describes the velocity distribution (assumed Maxwellian) of the bulk of gas which is being observed. There is also the temperature of the radiation field which bathes the molecule T_{rad} . The grains may be at yet another temperature.

The number density. As a telescope can only see an object in plan the length of the active volume is never known exactly. As a consequence in a simple case such as that governed by Eq. (1) only the column density nl (cm^{-2}) is obtainable directly. It is usual however to assume that a cloud is about as deep as it is wide and so derive an estimate of the number density n (cm^{-3}).

Cloud velocities. Along the line of sight there may be several pockets of gas each with its own characteristic set of temperatures and travelling with either the same or different mean bulk velocities relative to the observer. The velocity relative to the observed is called v_{LSR} the radial velocity relative to the local standard of rest (LSR). The frequencies (ω) will thus be shifted (by $\Delta\omega$) according to the Doppler relation, $\Delta\omega = (v_{LSR}/c)\omega$. Each pocket of gas will thus contribute some roughly gaussian line shape to an overall intensity/velocity line profile which may or may not be susceptible to deconvolution. Collisions are so infrequent in general that the pressure broadening mechanism that gives Lorentzian line shapes to microwave lines in the laboratory (Townes and Schawlow, 1955) can be neglected.

The equation of radiative transfer

In some cases, and in radioastronomy in particular, the simple Beer-Lambert relation Eq. (1) is not sufficient and the more complete radiative transfer equation must be used. Consider a slice of active medium of thickness dx . Then

$$dI(\omega) = -\gamma(\omega)I(\omega) dx + \varepsilon(\omega) dx \quad (12)$$

The Beer-Lambert relation Eq. (1) is derived directly from the first R.H. term. The second is an additional term which takes spontaneous emission with coefficient $\varepsilon(\omega)$ into account. We can set $\gamma(\omega) dx = d\tau(\omega)$ (where $\tau(\omega)$ is called the optical depth) and take into account that at thermal equilibrium Kirchoff's law indicates that absorption and emission are equal, i.e.

$$\frac{\varepsilon(\omega)}{\gamma(\omega)} = B_\omega(T_{ex}) \quad (13)$$

where $B_\omega(T_{ex})$ is the Planck function

$$B_\omega(T_{ex}) = \frac{2h\omega^3}{c^2} \frac{1}{e^{h\omega/kT_{ex}} - 1} \quad (14)$$

We will take the easy way out and assume that temperature and therefore $B_\omega(T_{ex})$ are

independent of $\tau(\omega)$ and integrate Eq. (14) from $I_0(\omega)$, the incident intensity, to $I(\omega)$, the emergent intensity, and from $\tau(\omega) = 0 \rightarrow \tau(\omega)$ (i.e. the optical depth equivalent to $x = 0 \rightarrow l$ the length of the active volume). Thus

$$I(\omega) = I_0(\omega) e^{-\tau(\omega)} + B_\omega(T_{ex})(1 - e^{-\tau(\omega)}) \tag{15}$$

If the line is narrow and sits on top of a broad flat background which is independent of ω then setting $I_0(\omega) \rightarrow I_0$ the excess line intensity can be defined as

$$\Delta I(\omega) = I(\omega) - I_0 = (B_\omega(T_{ex}) - I_0)(1 - e^{-\tau(\omega)}) \tag{16}$$

In the Rayleigh-Jeans limit $h\omega \ll kT$ and thus Eq. (14) simplifies and allows the following definitions:

1. The excess line brightness temperature $T_L(\omega) = a\Delta I(\omega)$
2. The excitation temperature $T_{ex} = aB_\omega(T_{ex})$
3. The background brightness temperature $T_0 = aI_0$

where $a = (c^2/2\omega^2 k)$. As a consequence Eq. (16) becomes

$$T_L(\omega) = (T_{ex} - T_0)(1 - e^{-\tau(\omega)}) \tag{17}$$

In general $T_0 = T_S + T_{BB}$ where T_S is a background source contribution and T_{BB} is the Universal 3K blackbody radiation. The total line intensity is expressed by the total line brightness, T_L , an integral over the line shape

$$T_L = \int T_L(\omega) d\omega \tag{18}$$

There are two particularly important limiting cases

1. The optically thick case for which $\tau(\omega) \gg 1$ where the line brightness is independent of optical depth. In this case

$$T_L = T_{ex} - T_0 \tag{19}$$

and the brightness temperature gives the cloud excitation temperature directly and is independent of optical depth. It is essentially the case of a black body radiation which is independent of the material.

2. The optically thin case for which $\tau(\omega) \ll 1$ for which Eq. (17) becomes

$$T_L(\omega) = (T_{ex} - T_0)\tau(\omega) \tag{20}$$

In the simplest homogeneous cloud model in which $\gamma(\omega)$ is independent of cloud depth along the line of sight $\tau(\omega) = \gamma(\omega)l$ and so

$$T_B = (T_{ex} - T_0)l \int \gamma(\omega) d\Omega \tag{21}$$

From Eq. (2) and the following set of definitions and approximations for a linear molecule:

1. The line shape integral $\int S(\omega, \omega_0) d\omega = 1$
2. At LTE $(N_m - N_n) = N_m(h\omega/kT)$ for $h\omega \ll kT$
3. $N_m = (N/Q)(2J + 1) \exp[-hBJ(J + 1)/kT]$ where N is the total number density and Q the rotational partition function which $\approx kT/hB$ for the case where $hBJ(J + 1) \ll kT$ (Herzberg, 1950),

Eq. (21) becomes

$$T_B = \frac{8\pi^2}{3ck^2} \frac{T_{ex} - T_0}{T_{ex}^2} hB(2J + 1) Nl\omega^2 |\langle J|\mu|J - 1 \rangle|^2 e^{-E(J)/kT} \quad (22)$$

For a $J \rightarrow J - 1$ emission line

$$|\langle J|\mu|J - 1 \rangle|^2 = \mu^2 \left(\frac{J - 1}{2J + 1} \right) \quad (23)$$

A consequence of Eq. (19) is that in a case such as that of CO, where in general the $^{12}\text{C}^{16}\text{O}$ line is optically thick, T_{ex} is obtained directly from the brightness temperature. From T_B for $^{13}\text{C}^{16}\text{O}$, which is often optically thin, one can *then* obtain the column density Nl according to Eq. (22).

The excitation temperature T_{ex} results from a subtle blend of various factors which can affect the populations of the connected states. To determine this, *statistical equilibrium calculations* should be carried out. The simplest case of a two level system subject to collisions with a surrounding gas with kinetic temperature T_k and to radiation field characterized by temperature T_r has been studied by Purcell and Field (1956). In the simplest form

$$T_{ex} = (\tau_r T_k + \tau_c T_r) / (\tau_r + \tau_c) \quad (24)$$

(Rank, Townes and Welch, 1971) where τ_c is the collision lifetime and τ_r is the radiative lifetime. Winnewisser, Churchwell and Walmsley (1979) have discussed this problem in further detail with some appropriate examples.

Radioastronomy

Radiotelescopes are essentially glorified radios with large, steerable, highly directional aerials and expensive amplifying electronics, which can tune in to very weak sharp frequency signals. The modern parabolic reflector is, like an optical telescope, diffraction limited in that it can distinguish between beams from two sources separated by $\delta\theta \sim \lambda/D$ (in radians) where λ is the operating wavelength and D the diameter of the mirror. Theoretically the limit is governed by the *half power beam width HPBW*. For a parabolic reflector this is $HPBW = 1.22 \lambda/D$ radians. One can obtain higher spatial resolution by increasing D or by reducing λ , i.e. increasing the frequency. D can also effectively be increased by interferometric aperture synthesis techniques.

The way in which the radiation is processed depends on the frequency ranges and the particular philosophy of the telescope designers. In general the radiation from a distant source is collected and focused by a radiotelescope's parabolic reflector into a cooled parametric or maser amplifier (<100 GHz) or a Schottky barrier system (>100 GHz) located at the focal point. The focal point may be at the primary focus or a secondary mirror may be used to produce a secondary focus through a hole in the centre of the main reflector. In general the radiation having been amplified is converted to an intermediate frequency by a mixer, amplified further and detected. As the signal usually consists of a range of frequencies, the final stage is a spectrometer such as an electronic multichannel filter bank which can effectively analyse the signal and display it as a function of frequency. The data collection and processing is usually carried out by a computer as is the telescope pointing and guidance. A particular observation may consist of several hours of observations in which data is collected by tracking a particular source across the sky. During the observation some telescopes are designed to follow a continuous cycle in which they collect data from the source for a period say $\frac{1}{2}$ minute, jump off the source by a small

angle to a patch of clear sky for $\frac{1}{2}$ minute, and subtract this data from that in the on-source store. In doing so, instrumental and atmospheric features can often be continuously eliminated.

The signal is usually detected as an *antenna temperature* T_A which is a function of frequency and sometimes displayed as such. It is however more usual to display the spectrum as a T_A vs v_{LSR} , which can be determined if the laboratory rest frequency is known. In general the peak of the T_A vs v_{LSR} line shape will be the same for all molecules in the same cloud and so appropriate telescope frequency adjustment for the Doppler effect is straightforward.

If the cloud is an extended source i.e. its angular size is larger than the telescope's *HPBW* then the antenna temperature and cloud brightness temperature are the same i.e. $T_A = T_L$. If the cloud is smaller then so-called *beam dilution* occurs and $T_A = (\Omega_C/\Omega_A)T_L$ where Ω_C is the cloud solid angle and Ω_A is the antenna pattern acceptance solid angle (Winnewisser, Churchwell and Walmsley, 1979). As if the numerous temperatures met so far are not enough, there is yet another one, the *system noise temperature* T_{sys} . T_{sys} is the parameter that scales the random background noise level that occurs in any electronic system. In an ordinary amplifier this is the background hiss which determines the basic signal-to-noise level attainable. $T_{sys} \sim 50\text{--}80$ K at cm wavelengths and $300\text{--}1000$ K at mm wavelengths.

The signal-to-noise can be reduced as usual by integration as $T_{min} \propto t^{\frac{1}{2}}$ where T_{min} is the minimum detectable signal and t is the integration time. In practice, how long t is depends on a multitude of fairly obvious parameters, not least the strength of the line. CO can be detected using a 4 foot pocket instrument in the middle of New York and the signal in Fig. 21 of HC₇N after 6 hours of integration with a 46 m dish located ~ 200 miles away from civilization in Algonquin Park, Ontario to reduce interference.

Coordinates

Astronomical objects must be found by some sort of coordinate system. The usual ones are Right Ascension (RA or α) and Declination (Dec. or δ) defined in the first few pages of any introductory book on astronomy (*cf* Unsöld, 1977). A good example of these coordinates is shown in the map in Fig. 26 which should be compared with the photograph in Fig. 2. Most recent observations are specified with respect to the year 1950 which is usually specified on the diagrams, note however maps may differ in the reference year.

Useful astrophysical quantities

There are finally a few miscellaneous astronomical terms, definitions and facts that are useful in understanding the literature.

In this review distances have been given in light years (ly) which is of course the distance travelled by light ($c = 3 \times 10^{10}$ cm s⁻¹) in one year ($\sim 3.2 \times 10^7$ s) which is $\sim 9.46 \times 10^{17}$ cm or $\sim 10^{13}$ km. The main distinguishing feature between astronomers and the rest is that they give distances in parsecs (pc). One pc is the distance at which a star exhibits an angular parallax shift of one arc second against the background fixed stars (which are too distant to show any parallax) between two positions separated by 1 AU (Unsöld, 1977). $1 \text{ pc} = 3.086 \times 10^{13} \text{ km} \equiv 3.26 \text{ ly}$.

To get a feel for astrophysical distances it is worth noting that the radius of the Earth's orbit is $\sim 150 \times 10^6 \text{ km} \equiv 1$ astronomical unit (AU). Pluto's semi-major axis is $5.9 \times 10^9 \text{ km}$. Thus $R_{\text{Earth}} \sim 1.5 \times 10^{-5} \text{ ly}$. $R_{\text{Pluto}} \sim 40 \times R_{\text{Earth}} \sim 0.6 \times 10^{-3} \text{ ly}$. So the solar system can be considered to be contained in a volume of diameter $\sim 1/1000$ ly. The distance to the nearest star, Proxima Centauri, is $\sim 4.2 \text{ ly}$ and the distance to one of the nearest galaxies, Andromeda, is $\sim 2.2 \times 10^6 \text{ ly}$.

INTERSTELLAR SPECTRA

In this section the spectra of interstellar molecules are reviewed and salient points about certain molecules are highlighted individually. Electronic spectra are discussed first, followed by the radio detections and finally a short review of the recent infrared observations is presented.

Optical observations

There were a number of important conclusions to be drawn from the first spectroscopic observations in 1936–1940 of interstellar CH, CH⁺ and CN. The mere fact that molecules existed in such low pressure regions raised questions about how they were formed in the first place, apparently under conditions in which only binary collisions could occur. Indeed these observations instigated theoretical studies of interstellar molecule formation and the abundances of CH and CH⁺ still present problems (Dalgarno, 1976). It is thought that radiative association in which two molecules collide and the excess energy is carried away by a photon is one of the initial steps. The detection of molecules can be used to probe the physical and chemical conditions in the ISM. A nice example of the sort of information available at that time is highlighted in Fig. 13 where a collage of CN spectra is presented. The laboratory spectrum (Pearse and Gaydon, 1963) consists of vibrational progressions and sequences with associated *P*, *R* rotational fine structure (Herzberg, 1950). There are many transitions because under the excitation conditions a large number of rovibronic states are populated. In contrast the interstellar spectrum (Adams, 1941; Thaddeus 1972) shows only three lines *R*(0), *R*(1) and *P*(1) because only the two lowest rovibronic levels are significantly populated.

One can determine the rotational excitation temperature for CN very neatly from the ratio of the heights of the *R*(0) and *R*(1) lines in Fig. 13d. Assuming that $\gamma(\omega)l \ll 1$ and ω varies little from *R*(0) to *R*(1) then from Eqs. (1) and (2)

$$\frac{\Delta I(1)}{\Delta I(0)} = \frac{\gamma(1)}{\gamma(0)} = \frac{N(1) |\langle 2' | \mu | 1'' \rangle|^2}{N(0) |\langle 1' | \mu | 0'' \rangle|^2} \quad (25)$$

where the terms are defined by the values of J'' and the matrix elements are *electronic* matrix elements between the J' (upper electronic state) and J'' (lower electronic state). The J dependence of the matrix elements can be separated out and thus

$$|\langle J' | \mu | J'' \rangle|^2 = A(J' + J'' + 1) \quad (26)$$

(Herzberg, 1950, p. 126). From Fig. 13 we can estimate

$$\Delta I(1)/\Delta I(0) \sim 15.5 = 0.3226 \quad (27)$$

where 0.3226 is the line-height ratio. The energy separation between the $J'' = 0$ and 1 states is $2B_0'' = 113.5$ GHz and so assuming a Boltzmann relation for $N(1)/N(0)$ * the result is $T_{ex} = 2.98$ K. Thaddeus (1972) gives a value of 2.99 ± 0.06 from a careful analysis which, when corrected for instrumental factors (-0.06 K) and for electron collision excitation (-0.15 ± 0.08 K), is reduced to 2.78 ± 0.10 K.

An excitation temperature of 2.3 K had originally been determined from the intensities of these lines and had caused Herzberg (1950) to say it ‘... has of course only very

* $N_n = N_m e^{-\Delta E(\text{cm}^{-1})/0.6952T(\text{K})}$ or $N_m e^{-\Delta E(\text{GHz})/20.86T(\text{K})}$. Note that the M degeneracy, $(2J + 1)$, has been included in the matrix element and so is not included in this relation.

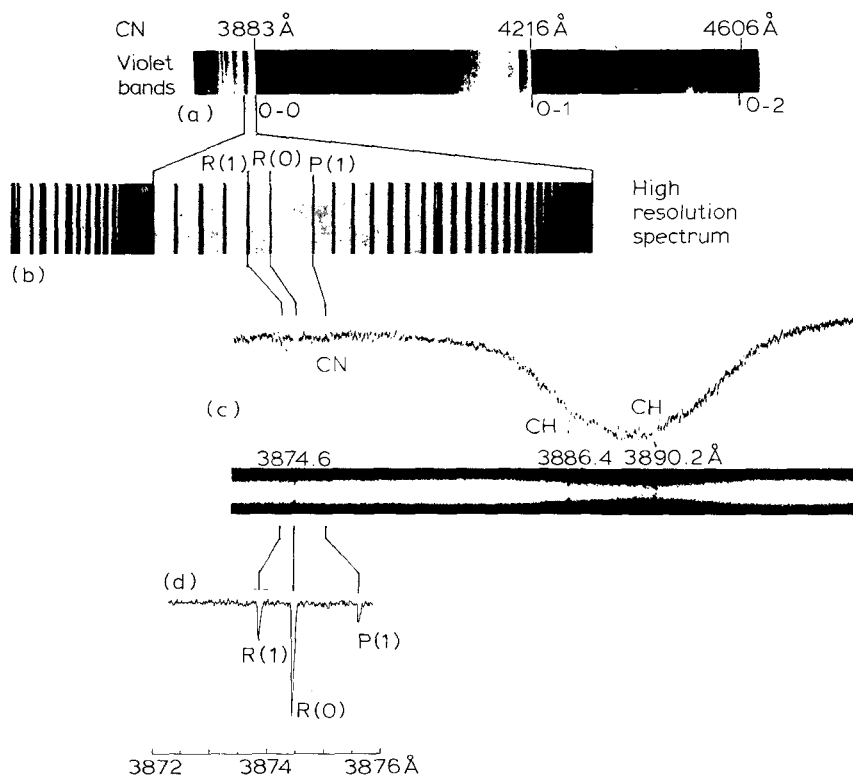


FIG. 13. A collage of CN spectra. (a) The low resolution spectra of hot CN observed in emission (taken from Pearse and Gaydon, 1963). These so called CN violet bands can be observed in a Bunsen burner flame. (b) The high resolution spectrum (from Herzberg, 1950) of the 0—0 band which has its origin near 3875 Å and P branch head at 3883 Å. Note the zero gap as this is a Σ — Σ transition for which Q branch transitions are forbidden. (c) The interstellar absorption spectrum of Adams (1941) shows the photograph below and the densitometer trace above. Lines of CH are also shown. The broad feature is absorption from H in the background star's atmosphere. (d) The spectrum obtained by Bortolot, Shulman and Thaddeus (1971), and given by Thaddeus (1972). In interstellar space the temperature is so low that only $J = 0$ and 1 levels are populated. This spectrum can be used to determine the temperature of the background radiation which is a relic of the Big Bang.

restricted meaning.' The restricted meaning is now recognized as one of the most important measurements on the three degree background which is perhaps the most persuasive piece of evidence in favour of the Big Bang theory of the origin of the Universe. In retrospect it is peculiar that this result was known before Gamow's 1948 estimate of the background temperature and not recognized (Alpher, Gamow and Herman, 1967; Thaddeus, 1972).

The early optical experiments were, of course, restricted to ground based observations and recent experiments have been carried out above the atmosphere allowing ultraviolet (2000 Å—4000 Å) and vacuum ultraviolet (<2000 Å) experiments to be carried out. Using a rocket-borne spectrometer absorption of starlight by diffuse interstellar clouds has finally revealed the most important interstellar molecule of all, H_2 . The Lyman Bands of

H_2 near 1092 Å have been detected by Carruthers (1971) and the Copernicus Satellite brought back further detailed results (Copernicus Satellite, 1973). The isotopic variant, HD, was also detected by Copernicus and these observations (Morton, 1975) and refined laboratory data (Dabrowski and Herzberg, 1976) are now compatible (Herzberg, 1980). The ratio of HD to H_2 appears to be $\sim 10^{-6}$ which is low compared with the terrestrial abundance of D/H $\sim 2 \times 10^{-4}$. This is probably because the low abundance of HD causes it to be less effectively self-shielded than is H_2 and thus more efficiently photodissociated in the diffuse ISM where it is observed.

Another important molecule has been added to the list of interstellar molecules by optical measurements. The molecule C_2 was detected by ground based spectroscopy at ~ 8750 Å, just in the infrared, by Souza and Lutz (1977). The study indicates column densities of $\sim 1.2 \times 10^{13} \text{ cm}^{-2}$ and $\tau_{\text{ex}} \sim 97 \text{ K}$ (Chafee *et al.*, 1980).

The diffuse interstellar lines which lie between 4400 and 6800 Å were also detected during the same period that CH, CH^+ and CN were observed. These are a set of broad diffuse absorption features, the first of which were detected by Merrill (1934). Since then more have been detected and there are now some 39 features whose characteristics have been reviewed by Wu (1972), Herbig (1975) and Smith, Snow and York (1977). They have now puzzled astronomers and spectroscopists for nearly five decades. The line strengths of the better observed features seem to show almost no relative variations and are thus thought to belong to a single carrier. It has been suggested that the lines belong to a molecule which might have predissociated structure or unresolved rotational structure (Herzberg, 1965, 1967).

It has also been suggested that the carrier is a constituent of solid grains perhaps matrix trapped impurities (Merrill and Wilson, 1938). A more recent suggestion by Douglas (1977) is that the bands belong to various C_n chain molecules. Suffice it to say that the identity is really no more certain today than it was when they were first detected and this puzzle remains one of the outstanding unsolved mysteries (*see Discussion*).

Radio spectra

OH

The detection of the 21 cm line of hydrogen in 1951 revolutionized galactic astronomy and for the first time the overall structure of our galaxy became apparent. Maps of H atom densities were made which delineated arm-like features similar to those in other spiral galaxies. An interesting point is that in studies of dark clouds such as Bok globules the H atom intensity tended to increase towards the feature and then decrease towards their interiors (Dickman, 1977)—a clear sign that in these clouds the hydrogen was in molecular form. The maximum H atom intensity tended to be $n_{\text{H}} \sim 1 \text{ cm}^{-3}$.

The existence of free radicals implied that species such as OH and NH might also be detectable and in fact OH has four Λ -doubling transitions close to 1660 MHz or 17 cm which were detected by Weinreb *et al.* (1963). These OH transitions have been subjected to a great deal of study and the situation as far as dark clouds are concerned was reviewed by Turner (1973) and also by Snyder (1972). The lines are seen in absorption in the galactic plane whenever there is an appropriate continuum background source. The transitions are also observed in emission, often with anomalously high intensity and sometimes fluctuating intensity and frequency. In particular the four lines at 1612, 1665, 1667 and 1720 MHz are expected to have relative intensities of 1:5:9:1. These ratios are seldom observed which indicates non-equilibrium excitation. The high brightness temperature often observed from very compact regions indicates that special excitation conditions are pumping maser emission (Moran, 1976).

The situation is very complicated because this ubiquitous molecule is observed in absorption throughout the galactic plane and in emission associated with almost any source of pumping radiation such as IR stars and HII regions as well as dark clouds (Snyder, 1972). These data have been the subject of numerous theoretical treatments aimed at understanding the pumping mechanism. To some extent, the complexity of the overall picture obtained from the OH studies makes it very difficult to draw general conclusions about the ISM. However, because of the often high intensity it does allow some of the highest resolution maps to be made. A most important early result was the occasional observation of an *anticorrelation* with H 21 cm radiation and a correlation with dust clouds, the first real evidence that molecules were indeed lurking in these secluded regions of the ISM.

Stable molecules

The ammonia molecule, which was the decisive key (Cheung *et al.*, 1968, 1969) in opening up this subject in 1968, is an oblate symmetric top whose levels are complicated by inversion splittings as shown in Fig. 14. Interaction between inversion and rotation causes

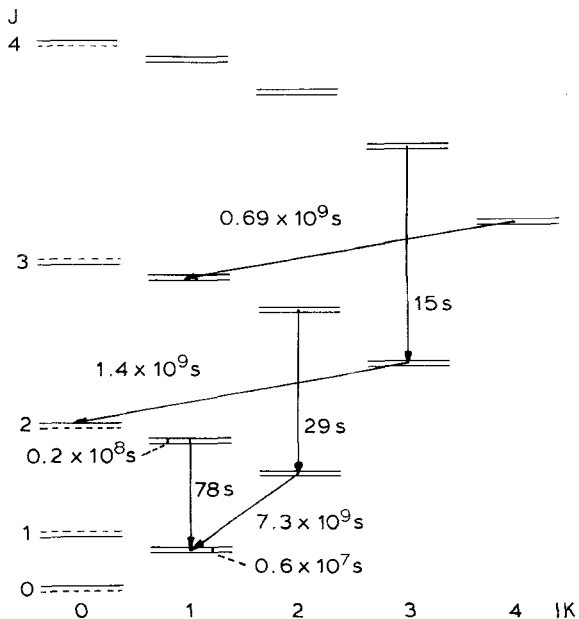


FIG. 14. The energy level pattern of the NH₃ molecule which is an oblate symmetric top ($B = 298$ GHz; $C = 189$ GHz) with inversion splitting of 24 GHz. Note that for $K = 0$ only one of the inversion levels occurs due to spin statistics and that transitions between *ortho* NH₃ with $|K|$ a multiple of 3 and the rest (*para* NH₃) do not occur. Completely allowed transitions occur only with $\Delta K = 0$ and $\Delta J = \pm 1$ and between inversion split levels. The radiative lifetimes of these are ~ 10 – 100 s and $\sim 10^7$ s respectively. Transitions with $\Delta K \neq 0$ which are strongly forbidden, can occur within the *ortho* and *para* manifolds with $\tau_{\text{rad}} \sim 10^9$ – 10^{10} s (Oka *et al.*, 1971). As a consequence of these τ s excited NH₃ cascades radiatively very quickly down a $|K|$ manifold to the lowest $J = |K|$ state which is metastable. Note also that the states are split further by very small hyperfine interactions which are not shown.

the various inversion transitions to lie at slightly different frequencies near 24 GHz (Costain, 1951). Transitions may also occur between the various J levels; these lie at much higher and less accessible frequencies but they are important in the overall population conditions. A most valuable aspect of the inversion transition is the proximity of the frequencies for different J and $|K|$. This allows their relative intensities to be studied with one telescope (Fig. 15) so requiring minimal correction in deriving population factors from the relative intensities. The populations are governed by the radiative lifetimes: $\tau_{\text{rad}} \sim 10^9$ s for $\Delta K \neq 0$ transitions and $\tau_{\text{rad}} \sim 10\text{--}100$ s for $\Delta K = 0$ (Oka *et al.*, 1972; Sweitzer, 1978). Consequently the lowest J levels for a given $|K|$ are metastable. This factor is critical in analysis of the collision and radioactive energy distribution mechanisms.

The care with which line intensities must be treated is exemplified by important results on NH_3 in SgrB2 of Winnewisser, Churchwell and Walmsley (1979a) who showed that lines in emission at low resolution had major absorption components when studied with

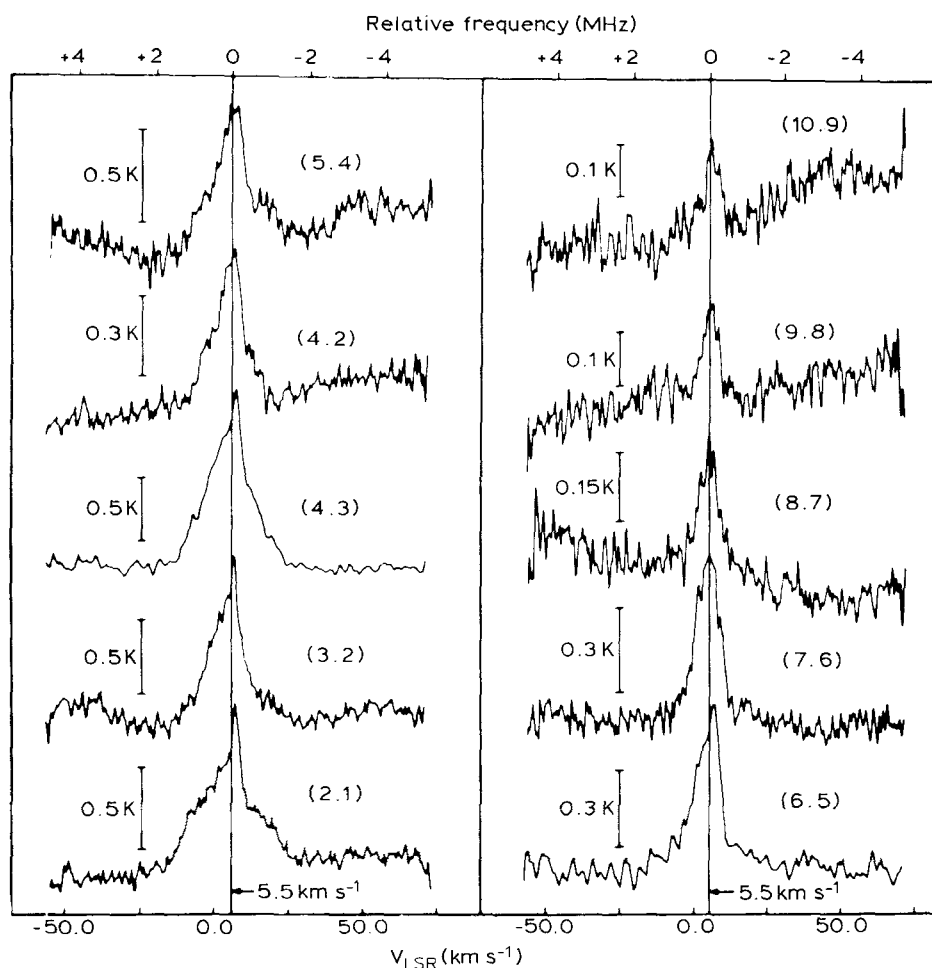


FIG. 15. The $(J, |K|)$ inversion transitions of NH_3 in Orion KL from *non-metastable* levels observed by Morris, Palmer and Zuckerman (1980). The (10, 9) levels lie at more than 1000 K above the ground state and their detection implies a hot ($T_{\text{ex}} \geq 220$ K) dense ($n_{\text{H}_2} \sim 10^7 \text{ cm}^{-3}$) region in KL.

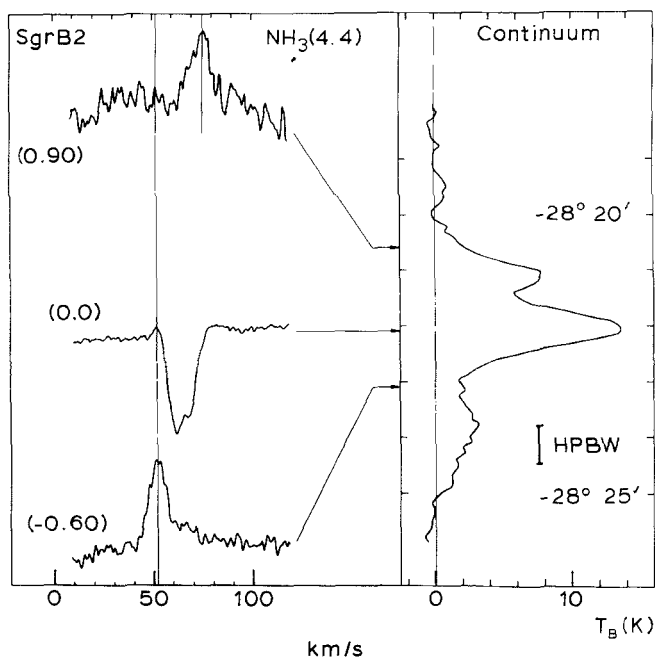


FIG. 16. An example of a complex excitation region in SgrB2 observed by Walmsley, Winnewisser and Churchwell (1979). With a $40''$ hpbw the transition is observed in absorption towards the continuum peak in SgrB2 (*centre*). In directions $90''$ N (*upper*) and $60''$ (*south*) the transition goes into emission. In previous lower resolution observations a single broad emission feature was observed (Morris *et al.*, 1973).

higher resolution (Fig. 16). In particular it indicates that complicated velocity structure and spatially inhomogeneous excitation conditions exist in this important molecular cloud. This makes it difficult to draw valid conclusions about the cloud's physical conditions (Winnewisser, Churchwell and Walmsley, 1979).

As well as detecting NH_3 , Cheung *et al.* (1969) also detected H_2O . The line detected was one which is not absorbed by atmospheric water vapour but does require anomalous excitation conditions. In fact this particular line is often detected in association with the OH masers. The conditions for pumping OH and H_2O masers are however different because the relevant H_2O levels are much higher in the manifold (about 450 cm^{-1}) than are the lowest OH (ground state) levels. These types of maser are discussed by Snyder (1972) and Moran (1976).

Recently a low energy line of H_2O has been detected at 183 GHz using a 91 cm radio telescope on the Kuiper flying laboratory, a C141 Lockheed transport which can fly at sufficiently high altitude to reduce atmospheric absorption (Waters *et al.*, 1980; Townes, 1980).

Formaldehyde, H_2CO , which was discovered in 1969 by Snyder *et al.* (1969) was the first of a series of small organic molecules to be detected. The first transition observed was that between the upper and lower $K_A = 1$ levels for $J = 1$ i.e. the $1_{10}-1_{11}$ K -doubling transition. The frequency is obtained very simply from Eq. (9) with $J = K_A = 1$ and $B = 38\,834$ and $C = 34\,004$ MHz thus yielding $\Delta E = B - C = 4830$ MHz. The $2_{11}-2_{12}$ transition at $\Delta E = 3(B - C) = 14\,488$ MHz has also been detected, as have other transitions. It is important to note that radiative cascade does not occur between the *ortho*

and *para* species because these are spin forbidden processes. This is for the same reason that *ortho* \leftrightarrow *para* H_2 conversion is not readily achieved. It is possible that reactive collisions might cause the conversion. The *K*-doubling transitions are usually detected in absorption and in fact are often observed in absorption against the 3 K background. This originally perplexing observation indicates that there is some mechanism possibly an idiosyncratic collisional process (Townes and Cheung, 1969; Garrison *et al.*, 1975) cooling the molecules or more correctly the associated levels below the ambient temperature of the Universe. Formaldehyde is a relatively ubiquitous interstellar species (Chaisson, 1978). The abundance and the sensitivity of the spectrum to collision processes make H_2CO an important probe of the interstellar medium.

The early period around 1970 saw the development of more and more sensitive receivers and detectors able to observe at higher and higher frequencies. This improvement enabled the Bell Laboratories group to detect $J = 1 \rightarrow 0$ line of CO at 115 GHz (Wilson, Jefferts and Penzias, 1970). This line was found as soon as the receiver was switched on and in fact CO is now known to be the most abundant molecule after H_2 . It is some 1000 times more abundant than any other species so far detected. The line is often optically thick and so, as discussed earlier, the line can be used to determine T_{ex} . The lines of $^{13}C^{16}O$, $^{12}C^{18}O$, $^{12}C^{17}O$ and $^{13}C^{18}O$ have also been detected. In cases where $^{13}C^{16}O$ is optically thin it is usually used to determine the column density. In Fig. 17 typical spectra, exhibiting complex velocity structure, obtained for ^{12}CO and ^{13}CO by Solomon, Scoville and Sanders (1980) in a direction in the galactic plane are shown. The relative intensities show clearly that ^{12}CO emission is optically thick.

A great deal of work has now been carried out with this line and the most important result is that the ratio $n_{CO}/n_{H_2} \sim 10^{-4}$ and appears to be very constant throughout the galaxy. A critical question is the ratio of $^{12}C^{16}O/^{13}C^{16}O$ and, as we shall see, this is not necessarily a good measure of the cosmic $^{12}C/^{13}C$ ratio. This is an important question because CO is now the most reliable way of determining the mass of H_2 because the emission is pumped directly and specifically by CO/H_2 collisions (Solomon, 1973).

Thus at present the best way of determining the mass of interstellar H_2 in the galaxy, its location and its density distribution is via the ubiquitous CO emission (Gordon and Burton, 1979). Its abundance is due to the stability of the strong triple bond towards

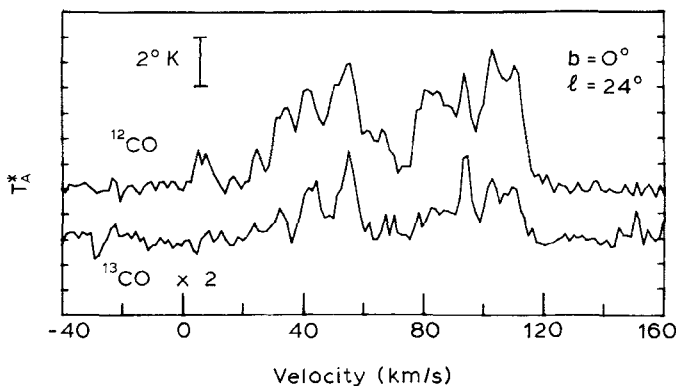


FIG. 17. Velocity structure in ^{12}CO and ^{13}CO emission in the galactic plane observed by Solomon, Scoville and Sanders (1980). Note that strength of the ^{13}CO relative to ^{12}CO which indicates that ^{12}CO emission is optically thick. Note also that the complicated structure of ^{12}CO is mimicked by ^{13}CO indicating that it is reliable data on which to base maps of CO abundance.

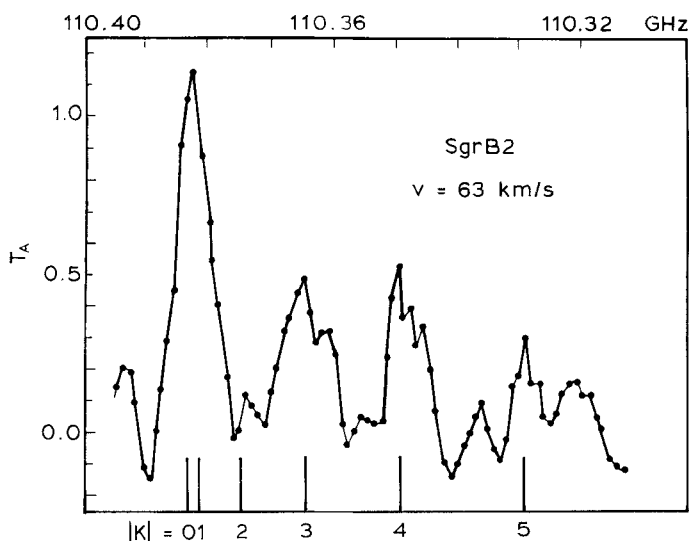


FIG. 18. The radio spectra of CH_3CN observed by Solomon *et al.* (1971). Comparison with Fig. 10 indicates that non-LTE conditions prevail.

photodissociation ($D_0 \sim 12$ eV). As important as its widespread detectability is the subtle balance that exists between its rotational radiative lifetime and the collisional pumping process with H_2 (Solomon, 1973).

The spectrum of methyl cyanide detected by Solomon *et al.* (1971) and depicted in Fig. 18 shows a clear example of non-LTE (local thermal equilibrium) effects. A comparison with the symmetric top laboratory spectrum shown in Fig. 10 indicates that if LTE conditions prevailed the $|K| = 2$ line should be somewhat stronger and $|K| = 4$ would be expected to be weaker. The presence of the high $|K|$ lines indicates a kinetic temperature of ~ 150 K and $n_{\text{H}_2} \sim 10^6 \text{ cm}^{-3}$.

The radio spectrum of the $J = 11 \rightarrow 10$ transition of ethyl cyanide, $\text{CH}_3\text{CH}_2\text{CN}$, observed by Johnson *et al.* (1977) is shown in Fig. 19 where it is compared with the expected structure. This is part of the central high K_A structure similar to that in the centre of Fig. 8. This spectrum shows structure which can leave no doubt as to the reliability of the assignment. The molecule $\text{CH}_3\text{CH}_2\text{CN}$ is actually one of the most complex so far detected and is related by hydrogenation to $\text{HC}\equiv\text{C}-\text{C}\equiv\text{N}$ via $\text{CH}_2=\text{CHC}\equiv\text{N}$. A careful comparison of these three molecules and their possible synthetic pathways in the laboratory and the ISM should yield some clues to the validities of the alternative chemistries that have been proposed for the ISM.

Methane, CH_4 , has a rotational spectrum predicted by Watson (1971) and detected by Rosenberg, Ozier and Kudian (1972). This spectrum should be very weak as it is caused by rotational distortion from tetrahedral symmetry, thus inducing a very small dipole moment of $\sim 10^{-5}$ Debye. Lines observed by Fox and Jennings (1978) in Orion have been assigned to CH_4 . These lines appear to differ from other interstellar lines in that they seem to vary in time and frequency, a behaviour ascribed to weak maser action.

In Fig. 20 is indicated a nice example obtained by Snyder, Johnson and Lovas (1976) of spectra from SgrB2, Orion A and W51 which indicates the variable physical and chemical compositions of three molecular clouds.

Several other stable molecules have been detected including such organic molecules as CH_3OH , CH_3SH , CH_3CHO , $\text{CH}_3\text{C}\equiv\text{CH}$, HCOOCH_3 and of course $\text{CH}_3\text{CH}_2\text{OH}$. Some

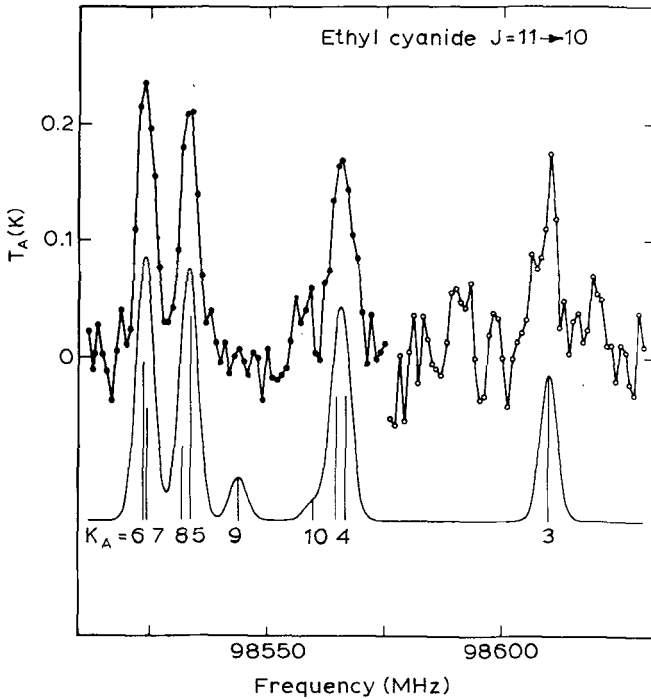


FIG. 19. The radio spectrum of ethyl cyanide $\text{CH}_3\text{CH}_2\text{CN}$ obtained by Johnson *et al.* (1977). This is part of the structure of the $J = 11 \rightarrow 10$ transition which tends to bunch together for an asymmetric top at high K_A . Compare with Fig. 8.

small inorganic species such as H_2S , SO_2 , SO have also been observed. Some, which are really intermediate between inorganic and organic such as NH_2CN , HCOOH and HNCO have also been observed. In fact it is highly likely that most molecules involving C, N, O and H which have any reasonable stability exist in the ISM. In Table 1 a list is presented and in Table 2 some estimated number densities are given.

In the next section the interstellar molecules which are stable because the physical conditions in the interstellar chemist's bucket differ dramatically from that of the bench chemist's are discussed.

TABLE 1. Observed interstellar molecules*

H_2	H_2O	NH_3	CH_4	CH_3NH_2	CH_3OCH_3
OH	H_2S	H_2CO	CH_2NH	CH_3CHO	$\text{CH}_3\text{CH}_2\text{OH}$
CH	HCO	H_2CS	NH_2CN	$\text{CH}_3\text{C}_2\text{H}$	HC_7N
CH^+	HCO^+	H_2C_2	HCOOH	CH_2CHCN	
C_2	HCN	HNCO	HC_3N	HC_5N	
CN	HNC	HNCS	HC_4		HC_9N
CO	HNO	C_3N		HCOOCH_3	
CO^+	HN_2^+		CH_3OH		
CS	HC_2		CH_3SH	$\text{CH}_3\text{C}_3\text{N}$	
NS	SO_2		NH_2CHO		
SO	OCS				
SiO					
SiS					

* also HOCO^+ or HOCN (see text). Molecules observed in circumstellar shells are also included.

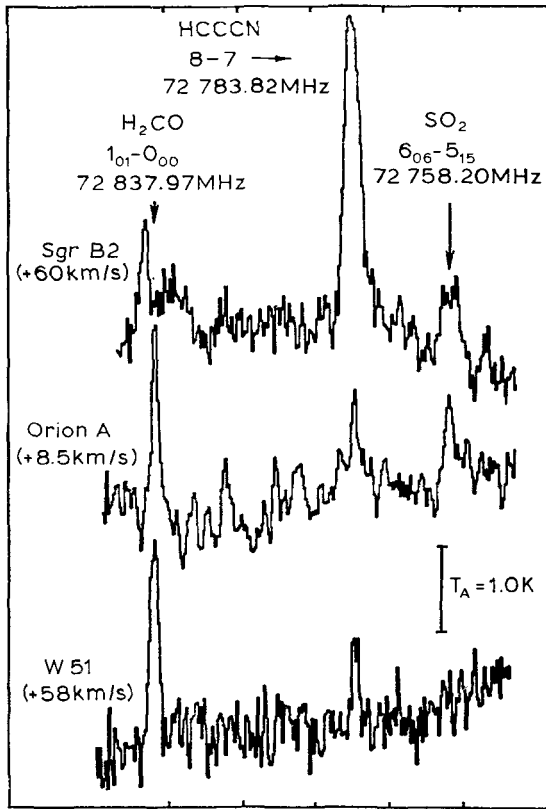


FIG. 20. Radiospectra from three molecular clouds showing clear differences between the clouds, however the results must be treated with care because the higher temperature in Orion means that the molecules are distributed among more levels. (Snyder, Johnson and Lovas, 1976).

TABLE 2. Fractional abundances of interstellar molecules*

R	Species				
1		H ₂			
10 ⁻⁴		CO			
10 ⁻⁶	HCN	HNC	NH ₃	SiO	SiS
10 ⁻⁷	OH	CS	SO	SO ₂	CH ₃ OH
	HCO ⁺	N ₂ H ⁺	C ₂ H	HCO	
10 ⁻⁸	CH	CN	NS	H ₂ CO	
	H ₂ S	OCS	H ₂ CO	HC ₃ N	
10 ⁻⁹	HNCO	CH ₃ C ₂ H			
10 ⁻¹⁰	H ₂ CS	CH ₂ NH	HCOOH	NH ₂ CHO	
	CH ₃ CHO	CH ₃ NH ₂	CH ₂ CHCN	HC ₃ N	
	CH ₃ C ₃ N	HCOOCH ₃	CH ₃ CH ₂ OH	CH ₃ OCH ₃	

* This table lists $R = n_x/n_H$, for the denser clouds where $n_H \sim 10^3 - 10^6 \text{ cm}^{-3}$. (Taken from Huntress, 1977).

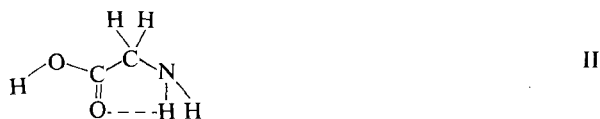
Unstable species

The conditions in the ISM ensure that once formed, molecules which react rapidly in the laboratory may be quite stable. After the initial phase of molecule detection which was in general governed by the availability of microwave data on known (mainly everyday) species an interesting interaction between astronomy and molecular spectroscopy began to appear. The realization that the interstellar conditions favoured some unusual and interesting species instigated and certainly encouraged the development of new spectroscopic techniques to study new molecules as well as others which are very difficult to handle in the laboratory. In this section some of the results of these investigations are discussed.

Glycine. A possible identification of interstellar glycine, $\text{H}_2\text{NCH}_2\text{COOH}$, the simplest amino acid, has been reported by Hollis *et al.* (1980) and the quest for this astrobiologically emotive species deserves discussion for various reasons. Microwave measurements on glycine originally yielded the spectrum of the conformer I in which



the hydroxyl H atom was H-bonded via the N lone pair as shown (Brown *et al.*, 1978; Suenram and Lovas, 1978). Subsequent radio searches for this species proved negative. Theoretical studies of the glycine potential surface by Vishveshwara and Pople (1977) and Sellers and Schäfer (1978) however indicated that a second conformer (II)



should be more stable than I by $\sim 350\text{ cm}^{-1}$. Suenram and Lovas (1980) subsequently detected the microwave spectrum of conformer II and on the basis of the laboratory measurements have identified one possible line (Hollis *et al.*, 1980). This detection requires further confirmation by for instance at least one line. One interesting point here is related to one made on page 326 with regard to the conformers of isocyanatoethene. The dipole moment of II appears to be 6 times smaller than that of I introducing a factor of $\sim \frac{1}{36}$ into the relative intensity via the dipole matrix elements in Eq. (2). This is the main reason why originally only I was detected in the laboratory, even though it is the less stable conformer. This is an enlightening example of the care with which microwave intensities must be treated.

The cyanopolyynes. An intriguing series of long linear molecules the cyanopolyynes, HC_nN (where n is an odd number), has been discovered. Hydrogen cyanide $\text{HC}\equiv\text{N}$ and cyanoethyne (cyanoacetylene) $\text{HC}\equiv\text{C}-\text{C}\equiv\text{N}$ which can be considered to be the first and second members in the series were discovered by Snyder and Buhl (1971) and Turner (1971) respectively. The next member of the series $\text{HC}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$ was synthesized and studied by microwave spectroscopy by Alexander, Kroto and Walton (1976) and its spectrum is shown in Fig. 5. The laboratory frequency was then used to detect the molecule in SgrB2 (Avery *et al.*, 1976). This discovery stimulated the synthesis of the next

member of the series, $\text{HC}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$, (Kirby, Kroto and Walton, 1980) and its subsequent detection in the cold quiet cloud in Taurus TMC1 by Kroto *et al.* (1978). This cloud had been identified by Churchwell, Winnewisser and Walmsley (1978), Little *et al.* (1978) and MacLeod, Avery and Broten (1979) as a cloud with an apparently high abundance of HC_3N (see page 357). The raw data for the original detection of HC_7N are presented in Fig. 21 and the laboratory spectrum is shown in Fig. 22. The comparison of these two spectra highlights vividly the advantages of low temperatures where all the molecules are in the ground vibrational state and each J transition shown in Fig. 22 is collapsed into a single intense line.

Having detected HC_7N the quest for the next member of the series, HC_9N , was initiated both experimentally and theoretically. A neat and simple extrapolation technique discovered by Oka (1978) was used to predict the B_0 value of HC_9N . Transitions remarkably close to the predicted positions were in fact detected by Broten *et al.* (1978) and in fact HC_9N was found in surprisingly high abundance in the cloud TMC1. HC_5N and HC_7N have also been detected in IRC10216 by Winnewisser and Walmsley (1978) (see page 355). The implications of these discoveries with regard to the chemistry of the ISM are discussed later.

This intriguing family of molecules has simple transitions which march systematically across the radio spectrum depositing convenient almost equidistantly spaced lines within the range of most receivers. In addition they have large dipole moments and intense *single* lines for a given J . Non-linear molecules have an extra (third) degree of freedom which causes the intensity associated with each J transition to be distributed among the members of the $|K|$ -multiplet in the case of symmetric tops (Fig. 10) and K_A -multiplet in the case of

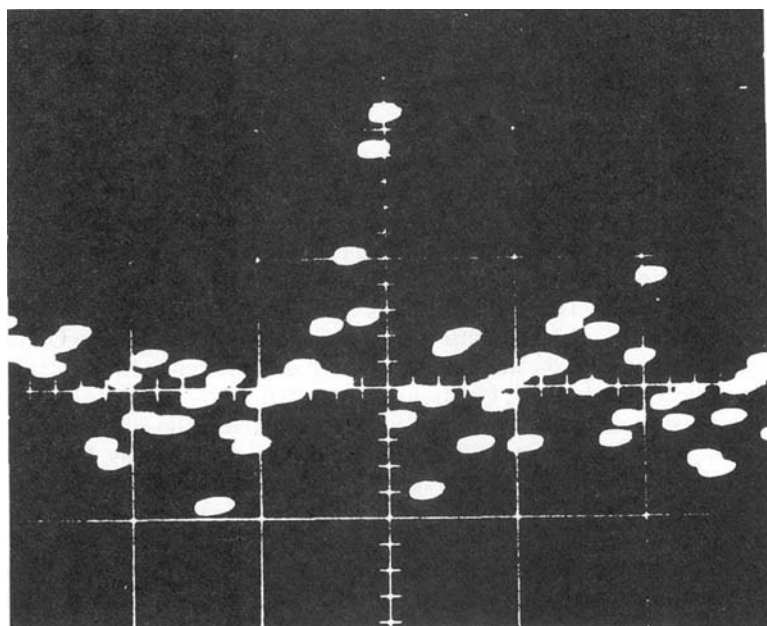


FIG. 21. A photograph of the raw data for the initial detection of $\text{HC}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$ (Kroto *et al.*, 1978), each dot represents data in a 10 kHz wide channel. The spectrum was observed from the cold cloud TMC1 which yields very narrow lines no more than 10 kHz wide. The range was centred so that the line should lie in one or two of the central three channels.

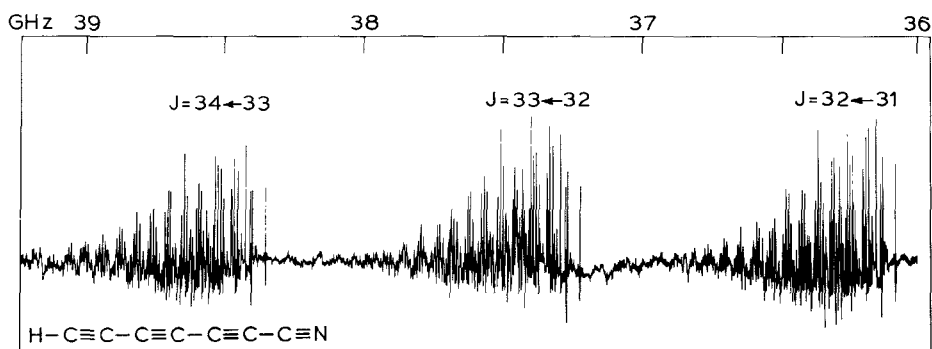


FIG. 22. Three members of the $J + 1 \leftarrow J$ rotational microwave spectrum of $\text{HC}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$ (Kirby, Kroto and Walton, 1980). The first RH line in each group belongs to the vibrational ground state, the rest are bending vibrational satellites and there are many of them. It is worth noting that there are six low to very low doubly degenerate bending modes each v 'th excited state is $v + 1$ fold degenerate and in addition there are combination levels. In cold clouds all the intensity crowds into the ground state line.

prolate asymmetric rotors (Fig. 8). In more complex molecules the intensity may be distributed in even more complex and widespread ways. The transitions of a linear molecule like HC_9N stand out like beacons amongst the multitude of weak lines associated with rotations of other large molecules. These properties have resulted in the quite active study of the cyanopolyynes with a view to obtaining important information on the structure of dense clouds, number densities, isotope fractionation and physical conditions (Avery, 1980; Tölle *et al.*, 1981; Benson and Myers, 1980). The molecules are found not only in SgrB2 and the clouds in Taurus but also in Orion (Morris, Snell and Vanden Bout, 1977) and elsewhere.

$\text{CH}_2=\text{S}$, $\text{CH}_2=\text{NH}$ and HNO . The detection of thioformaldehyde ($\text{CH}_2=\text{S}$) and methanimine ($\text{CH}_2=\text{NH}$) highlight some interesting aspects of the interaction between chemistry and astronomy in developing new techniques and results. These two isovalent species tend to be rather unstable under the usual laboratory conditions though they can be studied rather nicely under the low pressure conditions which are necessary for microwave measurements. They were produced in pyrolysis flow systems by Johnson, Powell and Kirchhoff (1971) and Johnson and Lovas (1972) respectively. On the basis of the frequencies determined in the laboratory for these *new* molecules the interstellar signals were detected (Sinclair *et al.*, 1973; Godfrey *et al.*, 1973).

Another molecule in this class of unstable species is HNO whose laboratory spectrum was detected by Saito and Takagi (1973). A weak line observed by Ulich, Hollis and Snyder (1977) has been assigned to this species. The weakness of the spectrum is in line with ion-molecule schemes which predict that molecules containing $\text{N}=\text{O}$ should not be abundant.

A few *free radicals* have been searched for and detected in the ISM by radioastronomy. Although no laboratory spectrum was known at the time Jefferts, Penzias and Wilson (1970) were able to detect interstellar CN on the basis of the approximate rotational and spin-doubling constants derived from the optical spectrum (Poletto and Rigutti, 1965). The laboratory microwave spectrum has now been observed (Dixon and Woods, 1977).

After a considerable amount of laboratory work culminating in an interferometric determination of the Λ -doubling frequency by Baird and Bredohl (1971) the *radio* spectrum of CH was finally detected by Rydbeck, Ellder and Irvine (1974) and Turner and

Zuckerman (1973). Another free radical that has been detected is NS (Kuiper *et al.*, 1975 and Gottlieb *et al.*, 1975). The laboratory spectrum was observed by Amano *et al.* (1969).

The microwave spectrum of the formyl radical HCO, detected in the laboratory by Bowater, Brown and Carrington (1971) and Saito (1972), has also been observed in the ISM by Snyder, Hollis and Ulich (1976).

The first ion studied by microwave spectroscopy was CO⁺ which was detected by Dixon and Woods (1975) in a discharge experiment. The resulting frequency measurements have been used to search for CO⁺ in the ISM and a possible assignment has recently been made for this elusive species by Erickson *et al.* (1981). CO⁺ should be much less abundant, by between one and three orders of magnitude, than is observed because of its rapid loss by reaction with H₂ to form HCO⁺.

The unidentified (U) lines. As the searches for interstellar lines continued, occasionally lines were detected accidentally which were not assignable to known species. The strengths of some of these U-lines (Snyder, 1972) were so great that they could only belong to small and stable (at least in the ISM) species. Klemperer (1970) suggested one of the lines detected by Buhl and Snyder (1970) might belong to HCO⁺. This intriguing conjecture has subsequently been verified by the detection of H¹³C¹⁶O⁺, H¹²C¹⁸O⁺ and D¹²C¹⁶O⁺ as well as by laboratory experiments carried out by Woods *et al.* (1975).

A search for HNC by Buhl and Snyder (1971, 1972) turned up a strong line at 90.7 GHz as a possible candidate. This line should have been split by nitrogen quadrupole interaction into a hyperfine triplet however the splitting was too small to be observed. This is to be expected as the quadrupole hyperfine splitting is smaller in isocyanides than in cyanides. Theoretical calculations (Booth and Murrell, 1972; Barsuhn, 1972) and the search for and detection of the laboratory spectrum simultaneously by Saykally *et al.* (1976), Blackman *et al.* (1976) and Cresswell *et al.* (1976) have nicely confirmed this assignment.

A group of three closely spaced U lines first detected by Turner (1974) was finally assigned to the $J = 1 \rightarrow 0$ transition of the linear protonated nitrogen ion HN₂⁺ by Green, Montgomery and Thaddeus (1974). The triplet structure was due to quadrupole splitting due to the end N atom. The central N atom which is in a location with a relatively small electric field gradient causes a very small further splitting. This splitting was almost resolved by Thaddeus and Turner (1975) in the spectrum of HN₂⁺ from the quiet cloud OMC2 (Orion Molecular Cloud 2).

A fourth molecule, the free radical C₂H, was also detected accidentally and assigned by similarly neat detective work. In this case a group of four lines (Fig. 23) which always tended to be detected together was first observed by Tucker, Kutner and Thaddeus (1974). The quartet was recognized as hyperfine structure due to a combination spin-rotation and nuclear spin/electron spin coupling, similar to that which occurs in the isoelectronic CN radical. The parameters which scale the latter interaction had already been determined by Graham, Dismuke and Weltner (1974) in matrix isolation e.s.r. experiments and convincingly verified the assignment. The transition actually consists of the four strong lines, which were first discovered, together with two weaker ones which were subsequently also detected at the frequencies predicted.

All four of these interesting molecules: HCO⁺, HNC, as well as HN₂⁺ (Saykally, 1976a) and C₂H (see Ziurys *et al.*, 1978) have been observed by Woods and others in the laboratory. The detection of these four unusual species is one of the more elegant stories in this always interesting field. These four molecules, perhaps more than any others, have lent great weight to the claims of the ion-molecule aficionados that their mechanism is the major one in the ISM.

Somewhat later Guélin and Thaddeus (1977) and Guélin, Green and Thaddeus (1978)

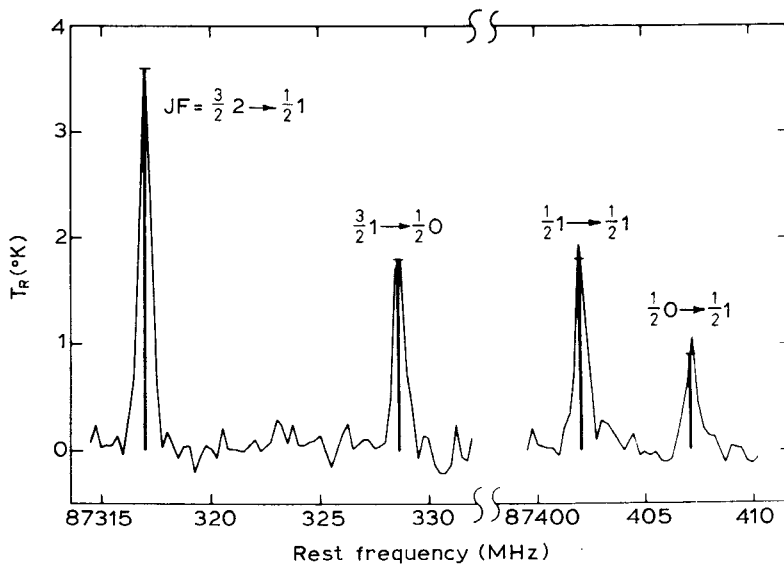


FIG. 23. Four of the six U-lines of the $J = 3/2 \rightarrow 1/2$ transitions of the free radical C_2H detected and identified by Tucker (Kutner and Thaddeus (1974)).

were able to add two more exciting species to this list, CCCN and CCCCH. These are both free radicals produced by abstracting H atoms from cyanoethyne and butadiyne respectively. Ab initio theoretical calculations played a useful part in the identification of these species (Wilson and Green, 1977). It is significant that these two molecules have until recently (Friberg *et al.*, 1980) only been detected in the circumstellar shell of the cool carbon star IRC + 10216 (*see* page 355) in which *no ions* have been detected.

Very recently Thaddeus, Guélin and Linke (1981) have identified interstellar HCS^+ and Gudeman *et al.* (1981) have detected its laboratory spectrum.

Thaddeus, Guélin and Linke (1981) have also presented strong evidence for the assignment of three U lines as the $J = 3, 4$ and 5 transitions of a linear molecule which is either $HOCO^+$ or $HOCN$. Detection of the lowest $J = 1 \leftarrow 0$, transition should allow differentiation between these two alternatives as the latter species should show N quadrupole hyperfine structure.

Winnewisser, Churchwell and Walmsley (1979) have surveyed the work on the various U line and free radical detections involving HCO^+ , HN_2^+ , HNC, HC_2 , HC_4 , C_3N , CN, CH and NS. Wilson (1980) has reviewed the applications of theoretical calculations to these and future assignments.

The list of unassigned lines is growing with time and attempts have been made to assign some of them (*see* for instance Rodriguez Kuiper *et al.*, 1977; Lovas, 1974; Kroto *et al.* 1978). A listing has been compiled by Turner (1979) of 120 or more.

Near and far infrared astronomy

Slowly but surely infrared techniques of sufficient sensitivity are being developed and they are yielding some of the most exciting recent results. The radio studies give detailed insights into the very cold and cool ISM and the electronic studies, insights into the very hot regions near to stars. At intermediate temperatures 500–5000 K various types of infrared emission are produced which give information about the conditions which exist

during the birth of stars. We now seem to be on the verge of observing the pre(nuclear)-ignition phase. In addition, the warm envelopes which surround cool (perhaps optically invisible) stars are becoming *visible* by infrared.

Recent reviews of infrared astronomy are given by Townes (1976, 1980) and Fazio (1976). Soifer and Pipher (1978) have discussed instrumentation and Merrill and Ridgway (1979) the infrared spectra from stars. Earlier reviews of infrared sources are given by Neugebauer, Becklin and Hyland (1971) and Neugebauer and Becklin (1973). Sufficiently sensitive techniques offering high enough resolution for molecule detection have been developing since about 1975. One of the major problems has been the atmospheric absorption. In some cases there are windows which allow work from ground level, but in many cases balloon platforms, high flying aircraft or very high mountain sites are utilized.

Using a Fourier transform spectrometer (Hall, 1976) together with the 4.3 m telescope at Kitt Peak absorptions by HCN, HC≡CH (Fig. 24) and CH₄ in the circumstellar shells of cool stars such as IRC + 10216 (Section 4) have been detected (Ridgway, Carbon and Hall 1978, Ridgway and Hall, 1980). Other molecules detected in stars by infrared are C₂, C₃, CH, CN, CO, CS, HCl, HCN, HF, H₂, H₂O, NH, OH and SiO (Merrill and Ridgway 1978).

An important breakthrough was made by Gautier *et al.* (1976) who were able to detect the quadrupole vibration rotation emission spectrum of molecular H₂ from Orion. In addition Beck, Lacey and Geballe (1979) have detected the pure quadrupole rotational emission of H₂ from the same region.

Townes and coworkers have been developing a wide range of new high resolution techniques aimed at opening up the whole infrared range (Townes, 1976). Watson *et al.* (1980) have detected the high *J* lines $J = 21 \leftarrow 20$ and $J = 22 \leftarrow 21$ lines from CO at about 1000 K in Orion (Fig. 25) indicating that the emission has been excited by a shock wave in the ISM (*see* page 352). These experiments were carried out using equipment mounted on a C141 Lockheed transport (the Kuiper Airborne Observatory) operated by NASA as a high altitude research platform. Storey, Watson and Townes (1981) have detected a direct rotational $J = \frac{5}{2} \rightarrow \frac{3}{2}$ transition of OH in SgrB2 using a tandem Fabry-Perot spectrometer on the Kuiper Airborne Observatory. The vibrational spectra of NH₃ (Betz, McLaren and Spears, 1979) and C₂H₄ (Betz, 1981) have also been recently detected in IRC + 10216.

The technical problems that have to be overcome to detect molecules such as HC≡CH, C₂H₄, H₂, etc. by far infrared techniques are considerable, they are however being overcome.

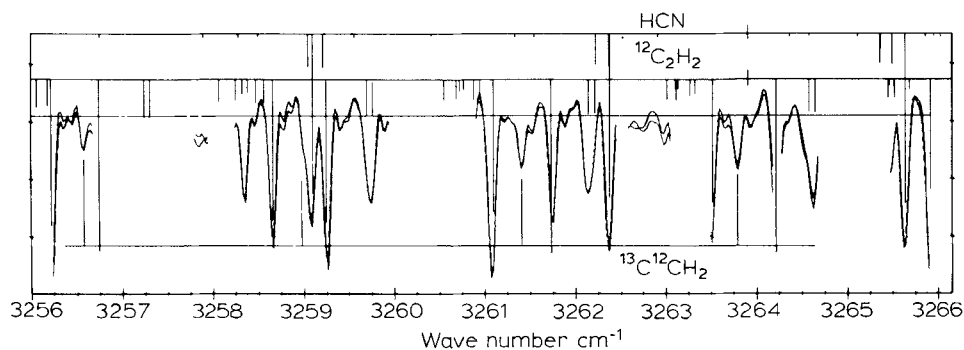


FIG. 24. The C—H stretching vibrational spectra of HC≡CH and H—C≡N detected by Ridgway, Carbon and Hall (1978) in the carbon star IRC+10216. The stick spectra are the predicted intensities for a temperature of 750 K. The lines are observed in absorption against the infrared continuum from the star itself.

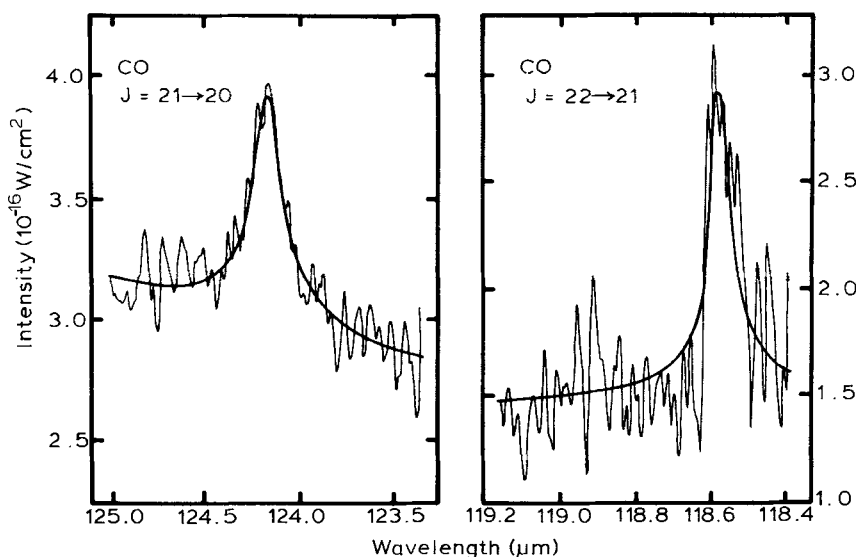


FIG. 25. Pure rotational emission lines of CO observed by Watson *et al.* (1980) using the Kuiper Airborne Laboratory. The emission originates from hot gas in and around the Kleinmann-Low infrared nebula. These lines lie just above those shown in Fig. 4.

Some specific interstellar sources

The Orion molecular clouds

Fig. 26 is a map of part of the sky in Orion taken from work by Kutner *et al.* (1977) which shows the extent of the stars, dust clouds and emission nebulae. The most familiar object is of course the Orion nebula (which has various aliases: Orion A, M42, NGC1976). Fig. 2 gives a good picture of what part of this region looks like. The well known Horsehead dark nebula shows up well as it is highlighted by the bright background HII region. The emission from Orion A is caused by the photoionizing radiation from a cluster of hot stars of which the four brightest form the Trapezium. Behind Orion A lies a molecular cloud, OMC1, within which resides a particularly dense, hot region roughly 1 ly further away than the Trapezium and just off the Trapezium line of sight. It is in this region that a cluster of infrared sources including the Kleinman-Low (KL) nebula and the Becklin-Neugebauer (BN) object are located. This region is at present being studied using every molecular probe available. The extent of the CO cloud is indicated in Fig. 26.

One of the first aims of the radio studies was to map objects such as the Orion cloud and compare their molecular compositions. These are of course two-dimensional maps of the radio intensity and care should be taken over their interpretation. Such a map is given in Fig. 27 (Turner and Thaddeus, 1977). It indicates that various molecules may not coexist and indeed it is not immediately obvious why N_2H^+ and HCO^+ do not have maxima in the same regions. Orion has been one of the two main hunting grounds for interstellar molecules and in general the molecules there have somewhat higher excitation temperatures than those in other colder regions. OMC1, which contains KL, has angular dimensions $\alpha \times \delta \sim 8' \times 4'$ and at the distance of Orion (1500 ly), $1'$ of arc ~ 0.5 ly so the cloud is $\sim 4 \times 2$ ly in plan. A second molecular cloud OMC2 lies about $10'$ (~ 5 ly) north

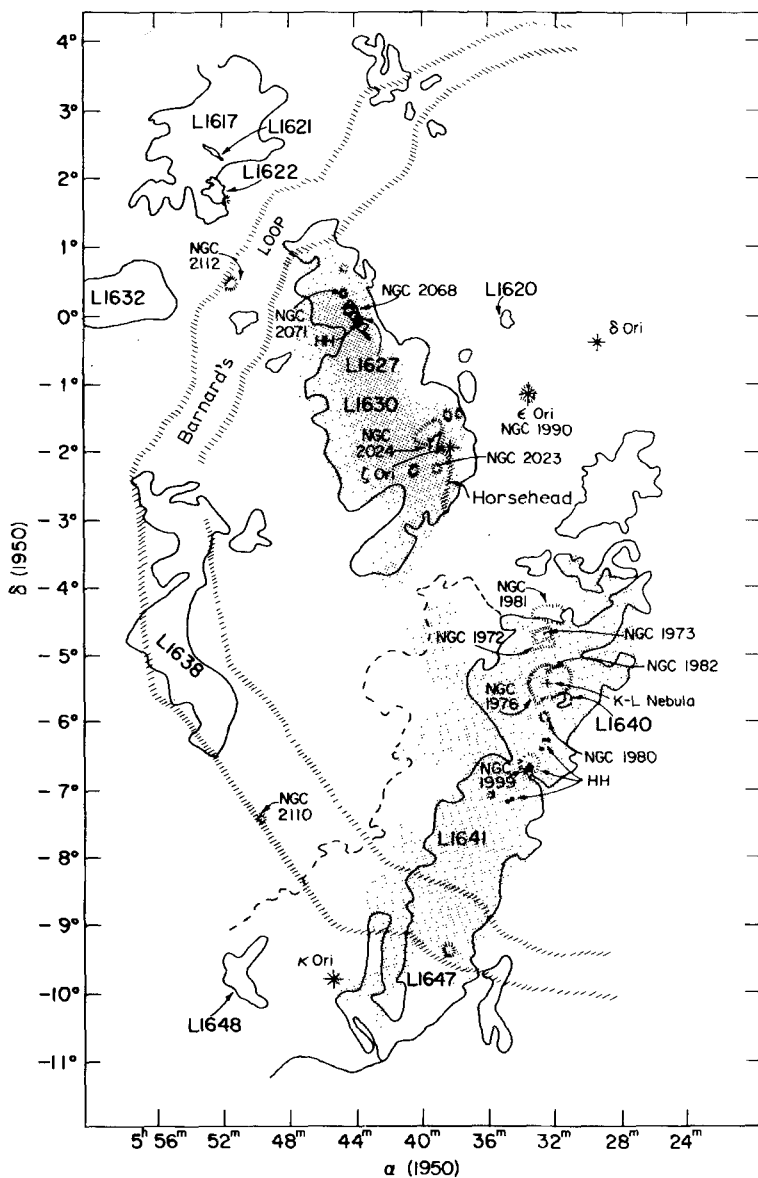


FIG. 26. Map of Orion given by Kutner *et al.* (1977). The three stars in the belt of Orion ζ , ϵ and δ Orionis are identified. The Orion nebula is NGC 1976. The Horsehead shown in Fig. 2 is also identified just south of ζ Ori. The hatched boundaries indicate boundaries of optical emission or reflection nebulosity. The approximate boundaries of dust clouds, designated by Lynds (L) numbers are given by solid lines; dashed line is a lower extinction edge of L1641. The dotted shading has been added to show the approximate extent of the CO emission from the Columbia (4 ft) observations. The emission peaks strongly at K-L and also near to ζ Orionis. The lower cloud which subtends ~ 7 degrees is roughly 180 ly long (Orion is ~ 1500 ly away).

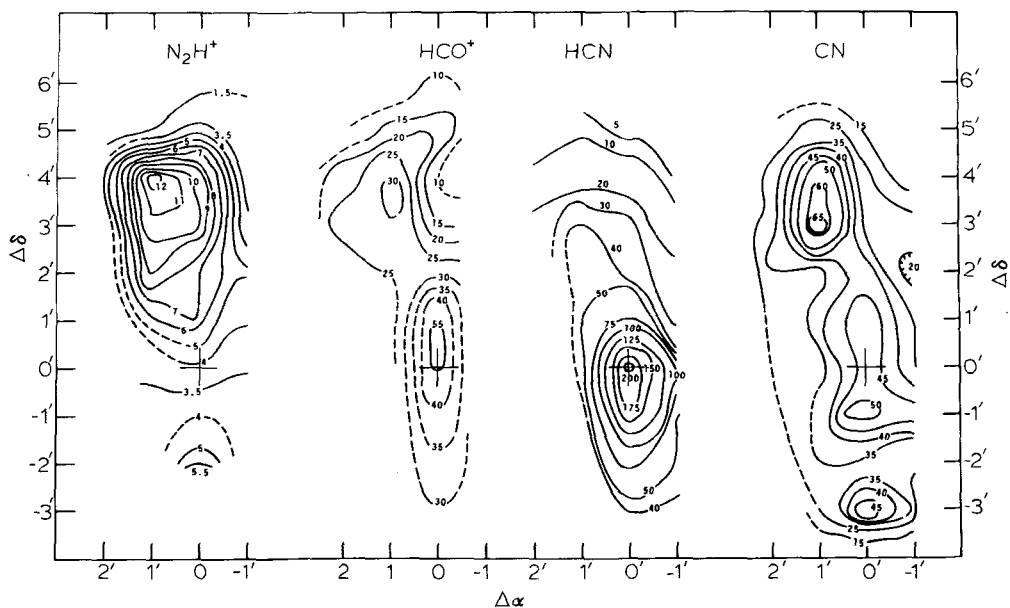


FIG. 27. Radio contour maps of integrated intensity for N_2H^+ , HCO^+ , HCN and CN published by Turner and Thaddeus (1977). The maps are all centred on K-L and show that the cloud is inhomogeneous in molecule distribution. In particular we see that HCO^+ has a maximum at a position where N_2H^+ has a minimum.

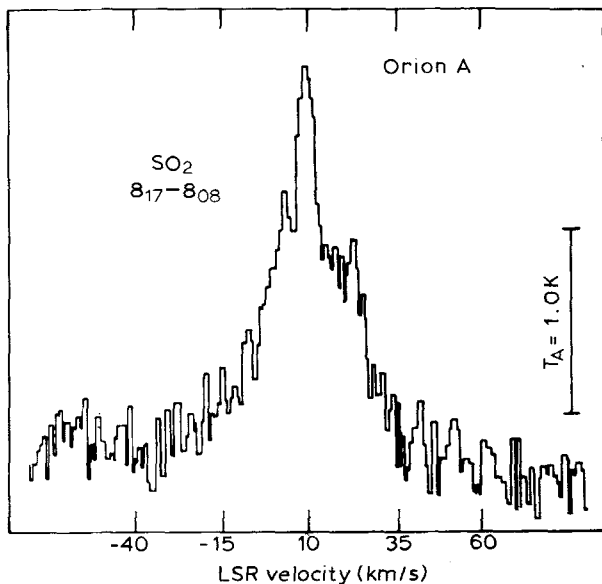


FIG. 28. The spectrum of SO_2 from Orion showing the two component characteristic: a wide plateau originating from KL and a narrow spike from the rest of the cloud.

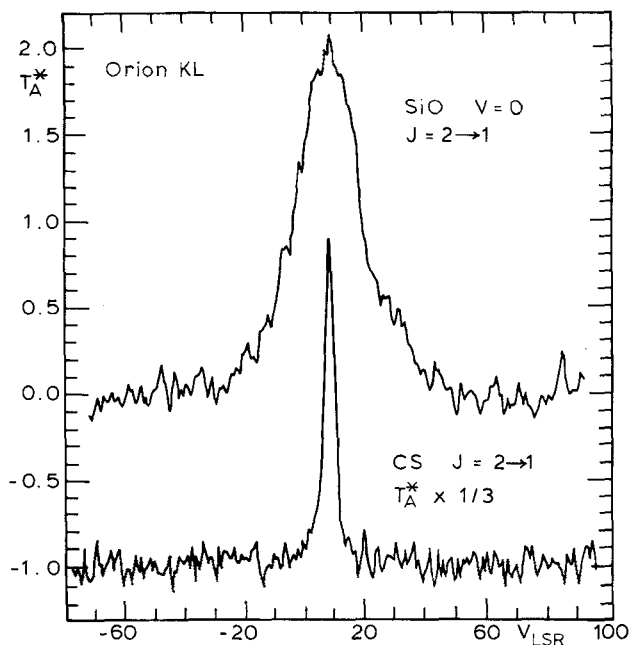


FIG. 29. The spectra of SiO and CS ($J = 2 \rightarrow 1$) emission from the KL nebula in Orion. The SiO line width is large which indicates it emanates from the high velocity core. The CS line is narrow indicating it resides mainly in the quiescent surrounding molecular cloud. Since these two molecules have similar excitation requirements the differences implies that SiO may have condensed out in grains by the time it gets into the cold surrounding cloud. From Scoville (1980).

of OMC1. OMC1 has a mass of $\sim 10^3 M_\odot$ and OMC1 and OMC2 together have a combined mass of $\sim 10^4 M_\odot$. The whole Orion GMC complex has a mass of $\sim 10^6 M_\odot$. The average kinetic temperature in OMC1 is ~ 70 K.

Radio linewidths towards KL often have a composite shape as shown in Fig. 28 for SO_2 . The wide plateau 30 km s^{-1} wide emission seems to come from an expanding warm cloud emanating from KL, whereas the sharp spike corresponds to emission from the OMC1 cloud itself. The comparison of SiO with CS from this same region Fig. 29 indicates that SiO appears only to have a plateau line shape and CS essentially only a spike. This may indicate that SiO is produced in some form of circumstellar type envelope and has condensed out into grains by the time it has reached the surrounding cooler and quiescent molecular cloud region.

The value of NH_3 due to the frequency proximity of various transitions with differing excitation requirements is indicated by the spectra in Fig. 15 obtained by Morris, Palmer and Zuckerman (1980). They show that these lines originate from a hot dense 220 K core with $n_{H_2} \sim 10^7 \text{ cm}^{-3}$ in KL. They interpret the data as emanating from a very young star i.e. a protostellar cloud on the verge of collapse.

Recent high spatial resolution molecular line aperture synthesis of this region has confirmed that the plateau is an expanding envelope centred on KL (Welch *et al.*, 1981). This type of study is certainly a most important direction for future molecular line work to follow.

The higher spatial resolution inherently available in the infrared due to the lower

diffraction limit is being exploited in the study of the KL/BN region of OMC 1. Beckwith *et al.* (1978) obtained the interesting map shown in Fig. 30 at 5'' resolution from their H₂ quadrupole emission studies. This should be compared with a 13'' resolution map (Beckwith *et al.*, 1978) and indicates how *qualitatively* different a picture can often be obtained with increased resolution. This is an instructive lesson in the care with which low resolution data should be treated. Beckwith *et al.* (1978) indicate that the emission emanates from a thin sheet, $\sim 10^{13}$ cm (or 10^{-5} ly) thick of H₂ gas heated to ~ 2000 K with a column density $\sim 10^{19}$ cm⁻². The source of excitation is not clear but a shockwave from a supernova explosion is possible. The CO ($v=4 \rightarrow 2$) vibrational emission near BN observed by Scoville *et al.* (1979) implies a compact collisionally excited region with $n_{\text{H}} > 10^{10}$ cm⁻³ and $T_{\text{ex}} \sim 3000\text{--}5000$ K. Airborne infrared experiments by Watson *et al.* (1980)

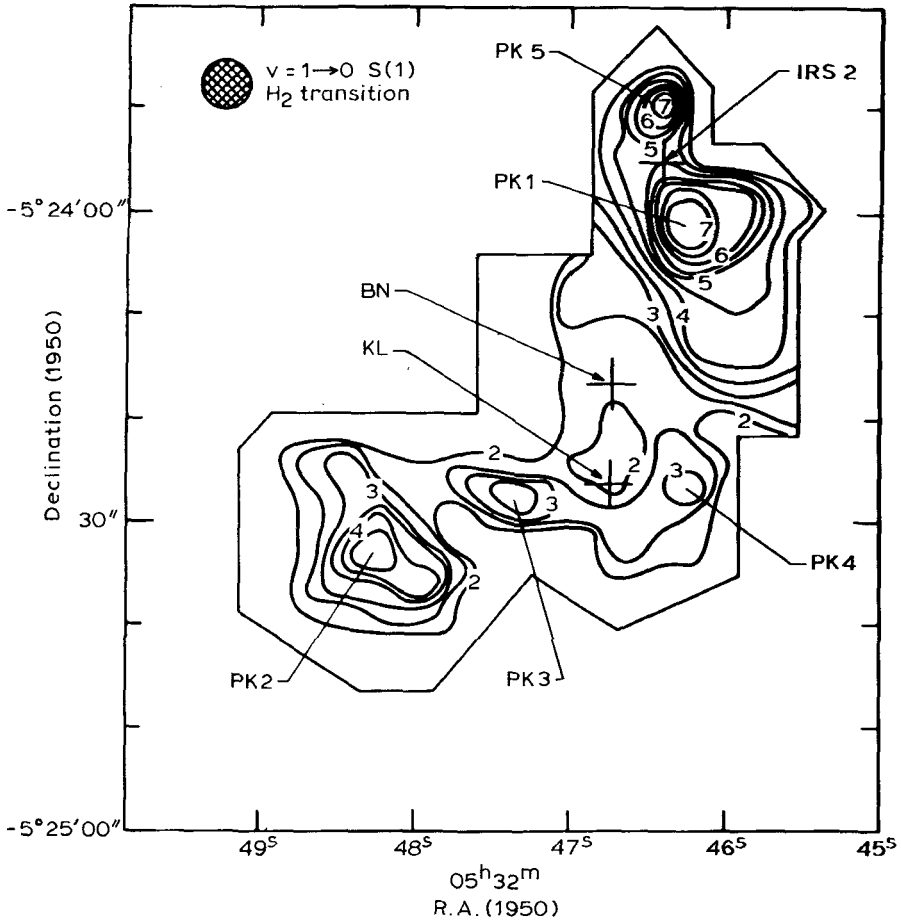


FIG. 30. Contour map of H₂ quadrupole vibrational emission at 5'' spatial resolution. At this resolution six peaks in the emission are detected and the picture changes quite considerably from a previous 13'' resolution map. From Beckwith *et al.* (1978). The emission arises from a thin (10^{-5} ly) sheet of hot (2000 K) H₂ gas perhaps heated by a shockwave from a supernova.

have succeeded in detecting strong $J = 21-20$ and $J = 22-21$ emission from post shocked gas at $T = 500-1000$ K in the region of KL (Fig. 25).

At present, the information we have about the convoluted activity in the murky depths of OMC1 may only be the tip of the iceberg as indicated by the recent detection of many new infrared sources in KL by Downes *et al.* (1981). With a great deal more dedicated study it should be possible to decipher the information being leaked out by the molecular moles in the core and so obtain detailed information on the birth of a star or indeed a cluster of stars.

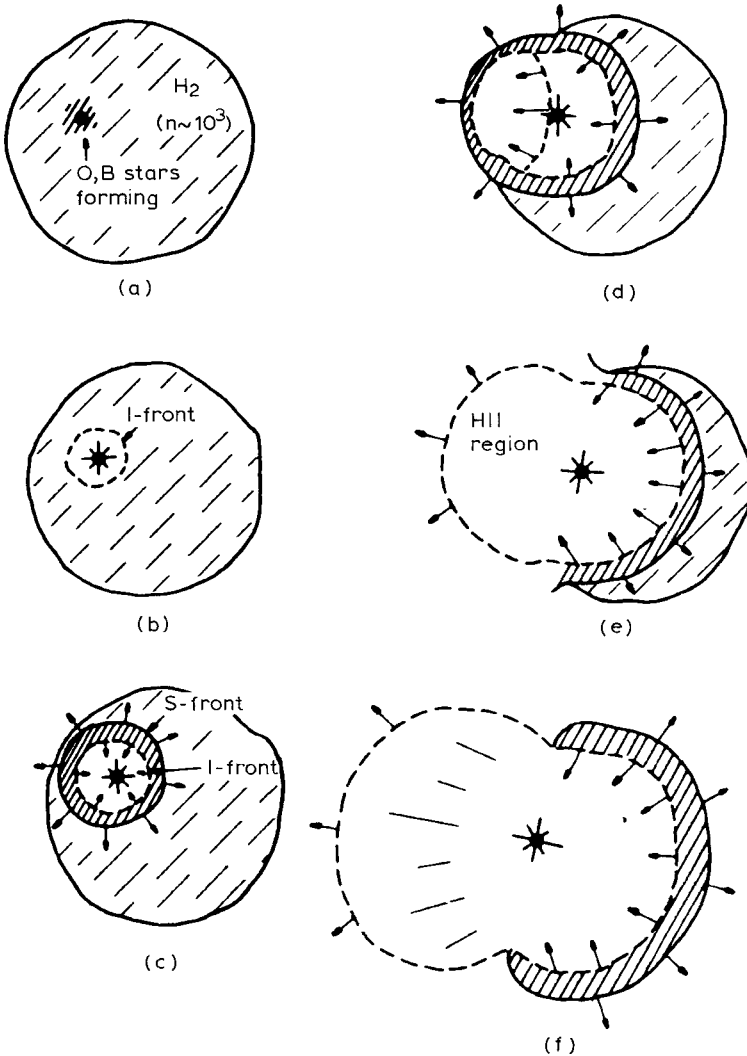


FIG. 31. A schematic diagram of the evolution of an HII region in a molecular cloud. Hot O and B stars form in the molecular cloud (a) and after some 3×10^6 years (f) the star becomes visible as the hot hydrogen blasts out of the molecular cloud. I indicates the ionization front and S the preceding shock front. This diagram is given by Bally and Scoville (1978) who suggest that the W80 complex of clouds and hot gas is in stage (f).

Thus we have a possible scenario for the Orion Nebula and a possible future one for the KLBN region similar to that presented in Fig. 31 by Bally and Scoville (1980) for the North American and Pelican Nebulae, W80. The Trapezium star cluster formed just inside the molecular cloud, and, once born, the hot O and B type stars ionized the surrounding molecular cloud. The resulting hot, high pressure HII region expands and sweeps up material behind a shock front. Eventually the HII bubble bursts through the surface to form the blister that we see optically as the Orion emission nebula and the stars become visible. The KLBN region may be the scene of a second performance which originates ~ 1 ly deeper in the molecular cloud. Perhaps at some time in the future (1000 years) the second bubble will burst and reveal the star or star cluster optically. Figure 31 shows how this may happen and how eventually the HII region might eat its way back through the rest of the cloud.

In Fig. 32 is given a schematic cross section of the Orion nebula and the molecular cloud behind it as suggested by Zuckerman (1973) and Zuckerman and Palmer (1974). This shows that the bright nebulae are essentially blisters which break out of the surface of molecular clouds (Chaisson, 1977).

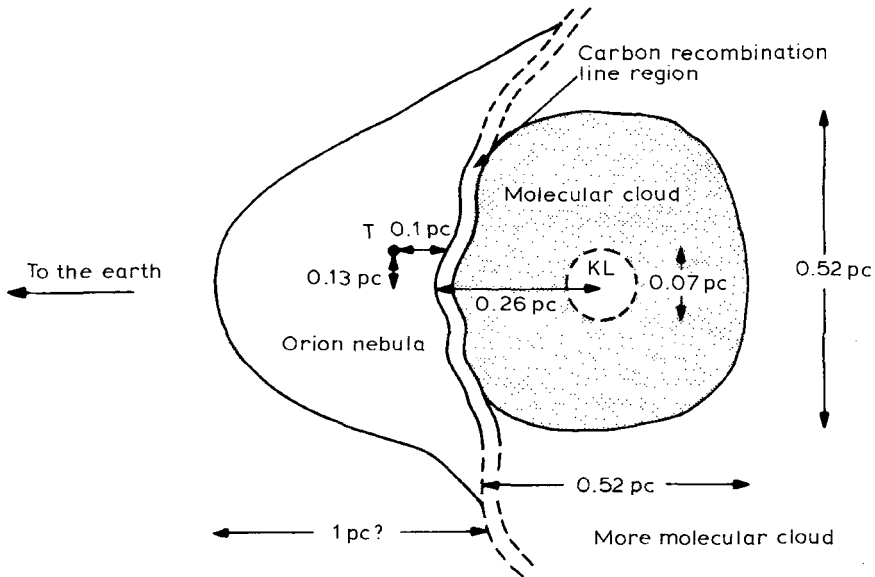


FIG. 32. A schematic cross sectional representation of a possible structure of the Orion nebula and the background molecular cloud as given by Zuckerman (1974).

SgrB2

The molecular soup with the most ingredients is the GMC, SgrB2, which lies some 30 000 ly away, very close to the centre of the Galaxy. Until recently every molecule detected had been observed in SgrB2. It is unfortunate that it is so far away because the distance limits our ability to probe the spatial fine structure. At this distance $1'$ arc $\equiv 10$ ly as compared with ~ 0.5 ly for Orion some 20 times nearer. SgrB2 is obscured by ~ 25 magnitudes* (a factor of 10^{10}) of scattering by interstellar dust. It has a dense core ($\sim 1' \equiv 10$ ly) surrounded by a less dense halo ($\sim 5' \equiv 50$ ly).

* 1 mag $\equiv 100^{1/5}$ —Astronomers (uncharacteristically) seem to use a magnitude factor smaller than other scientists i.e. 2.51 as opposed to 10.

Any deductions about the physical conditions in such a cloud must be treated with caution. A good example of the way in which misleading conclusions, on such matters as column density, can be drawn is shown in Fig. 16 where the complications in the line shapes of NH_3 transitions observed by Walmsley, Winniewisser and Churchwell (1979) are evident. At low resolution they appear to be essentially emission lines (Morris *et al.*, 1973) whereas at higher resolution the line is resolved into a more complex absorption/emission feature which implies a multicomponent cloud lies along the line of sight. The inhomogeneity of a cloud like SgrB2 can only be guessed at and it is known to contain several compact objects. The characteristics of SgrB2 and Orion have been reviewed by Winniewisser, Churchwell and Walmsley (1979).

IRC+10216

The variable infrared source IRC+10216 is a carbon star surrounded by an expanding dusty shell (Morris, 1975). The first molecule detected in the extended envelope was CO (Solomon *et al.*, 1971) and since then some 20 more have been observed. The line shapes depend on the optical thickness and whether the source is resolved or not. In Figs. 33 and 34 some examples are shown. In the radio studies one observes emission from the whole shell whereas in the infrared the absorption spectra use the star's infrared continuum emission as the background source and only the foreground part of the shell is detected (Ridgway and Hall, 1980). The results indicate that this and other objects such as CIT6 (Knapp, Kuiper and Zuckerman, 1979) are important molecule factories and there may be many more. The high spatial resolution infrared absorption results give information on the inner molecular component which is of the order of 1 AU in diameter. Ridgway and Hall (1980) have interpreted their infrared data shown in Fig. 34 as indicating a *double* expanding shell, an inner warm (300–700 K) shell expanding at 11 km/s and a cooler (150–250 K) outer shell expanding at 16 km/s.

Circumstellar absorptions due to CO, HCN, C_2H_2 and CH_4 have all been detected using a ground based infrared interferometer (Ridgway *et al.*, 1976; Ridgway, Carbon and Hall, 1978; Hall and Ridgway, 1978). Using an infrared heterodyne spectrometer on the

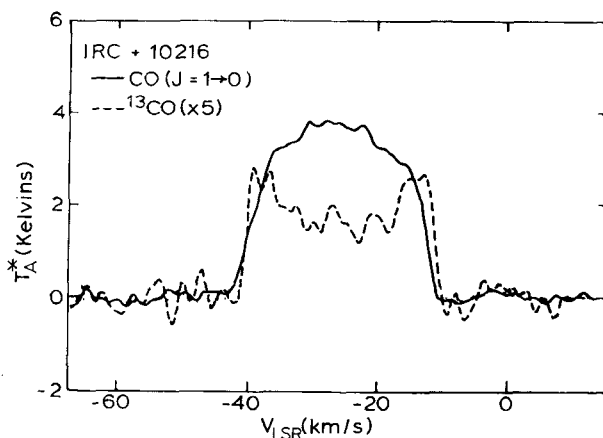


FIG. 33. Two examples of line shapes from IRC+10216. The $^{12}\text{C}^{16}\text{O}$ emission is optically thick and that of $^{13}\text{C}^{12}\text{O}$ is optically thin. The latter indicates quite nicely that two emission components, from sections at the front and back of the expanding molecular shell are being detected. *Half* the doppler velocity separations indicates the velocity of the outflowing gas. From Wannier and Linke (1978).

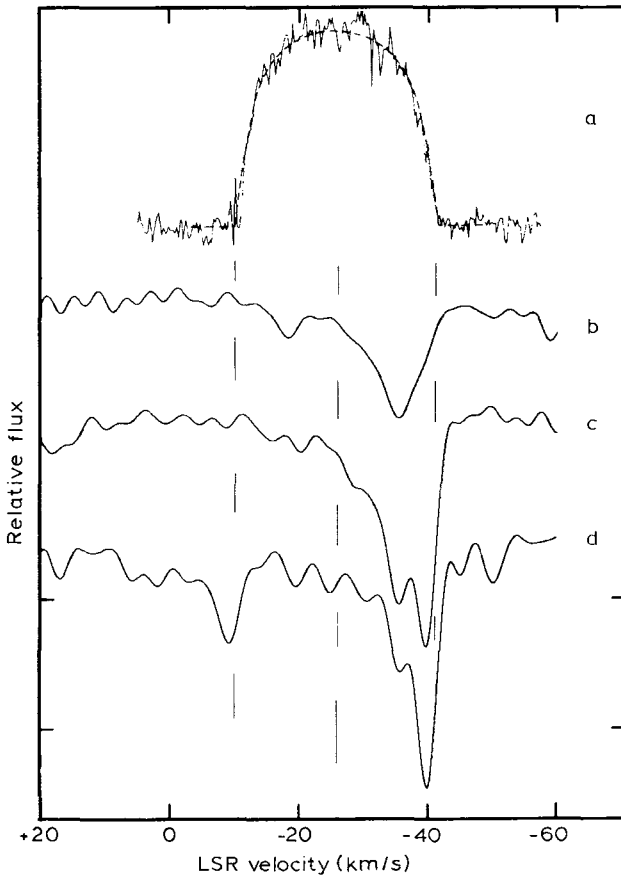


FIG. 34. CO line profiles in IRC+10216 (a) $J = 1 \rightarrow 0$ emission from Kuiper *et al.* (1976). (b) $v = 2-0$ absorption high excitation profile. (c) $v = 2-0$ absorption medium excitation profile. (d) $v = 2-0$ absorption low excitation profile. The clear doubling is interpreted as indicating a warm (300–700 K) inner shell expanding at 11 km/sec and a cooler (150–250 K) outer shell expanding at 16 km/sec. In all but (d) absorption is only observed from foreground gas. From Ridgway and Hall (1980).

Kitt Peak solar telescope Betz, McLaren and Spears (1979) have detected NH_3 and Betz (1981) has detected C_2H_4 .

Radio studies yield information about the more tenuous outer shell which has a diameter of ~ 1 ly apparently consisting of molecules being continually ejected in puffs from the inner regions. This is a clear example of molecules being injected into the general ISM.

The detections of the radicals C_4H and C_3N were made in this object (Guélin and Thaddeus, 1977; Guélin, Green and Thaddeus, 1978) and until recently not detected elsewhere. The detection of the long chain polyynes, HC_7N , in IRC+10216 (Winnewisser and Walmsley, 1978) may not be a coincidence. In addition it may be significant that no ions have been detected in IRC+10216. McCabe, Smith and Clegg (1979) have carried out a chemical equilibrium study to match the molecular abundances assuming a

freezing-in mechanism and have suggested that a compressed gaseous shell may be formed between the successive dust shells lost by the central star at each cycle.

It would be very interesting to discover more of these stars but so far IRC+10216 is by far the most well studied, mainly because it is the one of the brightest infrared objects. The interesting point is that apart from ions the same types of molecules appear to be observed being emitted from this star as are observed in some of the dense clouds.

Taurus molecular clouds

A particularly interesting region of dark clouds in Taurus is depicted in the beautiful photograph taken by Barnard (1927) (Fig. 35). This shows long black patches streaking across the sky obscuring the stars behind. Dotted around are also a few HII emission nebulae. Winnewisser, Churchwell and Walmsley (1979) have reviewed the radio studies in these types of dark clouds. Down near the left hand (SE) corner of this photograph lie the Taurus molecular clouds (TMC). TMC1, a molecular cloud buried in Heiles' cloud 2, in particular was found to be a very cold cloud (~ 10 K) with a high abundance of HC_3N (Morris *et al.*, 1976). In Fig. 36a a scale map of formaldehyde taken from that of Sume, Downes and Wilson (1975) is shown and Fig. 36b shows the appropriate region of Fig. 35

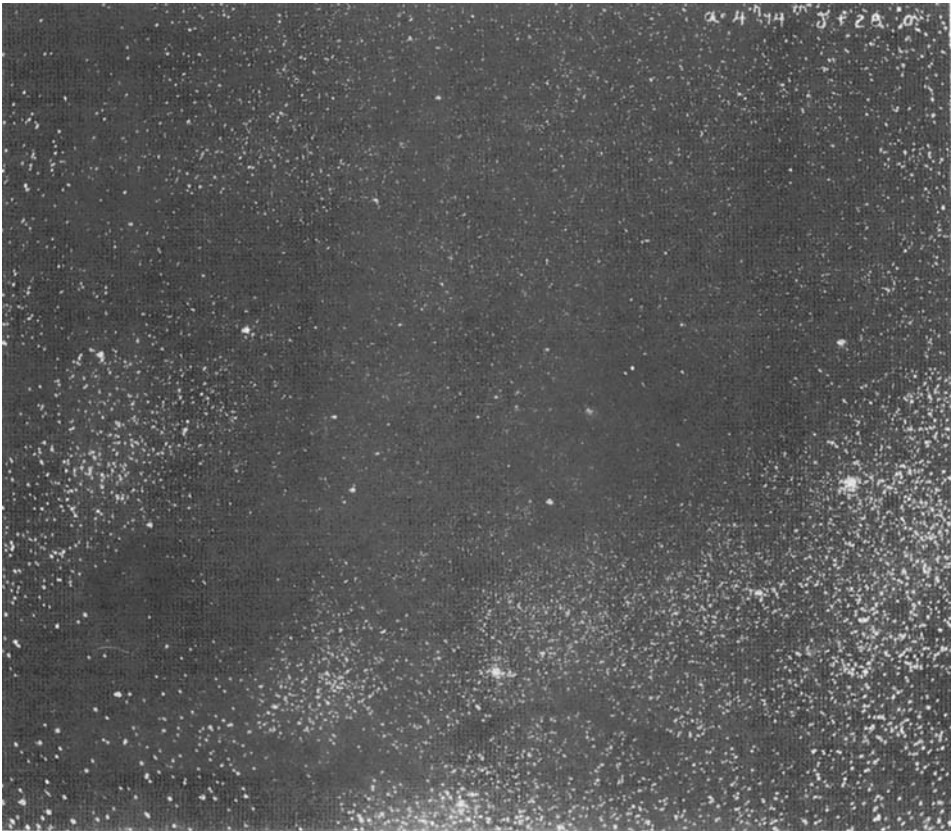


FIG. 35. The dark clouds in Taurus from Barnards (1927) Survey. The region of TMC1 is near the bottom LH (SE) corner and is shown to larger scale in Fig. 36.

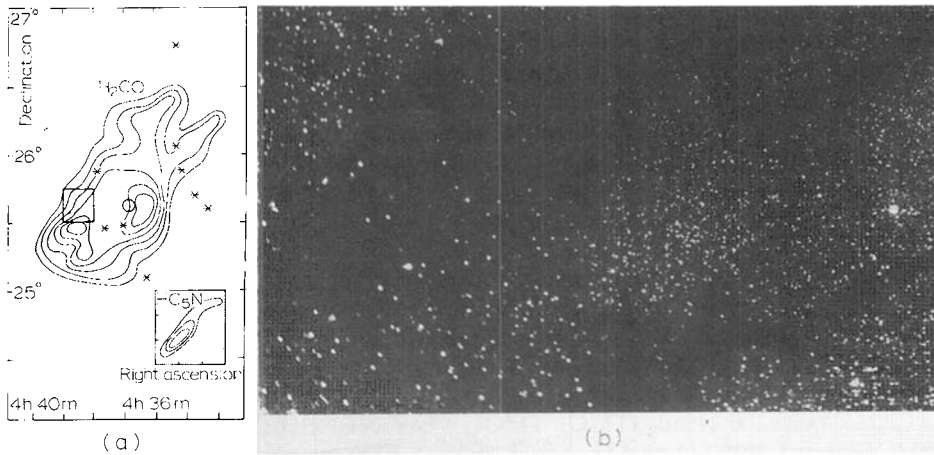


FIG. 36. (a) Shows a scale contour map of H_2CO from Sume, Downes and Wilson (1975). There is a minimum between the two H_2CO maxima which has been omitted. The inset shows the HC_5N map of Little *et al.* (1977) which has been enlarged and displaced from the square which lies on the side of the H_2CO cloud. This indicates the extent of the HC_5N cloud in TMC1. The left hand edge of the map coincides with the left hand edge of the photograph (b). There are two prominent stars near the map's centre.

expanded to scale. On the side of the formaldehyde hill, as indicated in Fig. 36, lies TMC1 and in the inset is given the HC_5N map of Little *et al.* (1978). This shows that the HC_5N cloud in TMC1 is an elongated ridge running from SE to NW with dimensions $\sim 10' \times 2' \cong 0.4 \times 0.08 \text{ pc} (\cong 1.2 \times 0.24 \text{ ly})$. The total mass of TMC1 appears to be $\sim 1 M_\odot$ (Myers, Ho and Benson, 1979). TMC1 has also been mapped in NH_3 and the NH_3 cloud appears to be rather similar in size, shape and orientation but displaced so that the maximum coincides with the NW tip of the HC_5N cloud (Avery, 1980). The C_2H map (Wooten, *see* Avery, 1980) has twin peaks coinciding with the NH_3 and HC_5N peaks. From HC_3N measurements TMC1 appears to consist of $1' \times 3'$ core ($T = 20 \text{ K}$) with $n_{\text{H}_2} \sim 6 \times 10^4 \text{ cm}^{-3}$ and $2.5' \times 10'$ halo ($T \sim 10 \text{ K}$) with $n_{\text{H}_2} \sim 10^4 \text{ cm}^{-3}$. The ratio $n_{\text{HC}_3\text{N}}/n_{\text{H}_2}$ is 3×10^{-9} in the core and 4×10^{-8} in the halo (Avery, 1980). The detection of HC_7N (Fig. 22; Kroto *et al.*, 1978) and also that of HC_9N (Brotten *et al.*, 1978) were both made at the HC_5N summit shown in Fig. 36a.

It is not at all clear whether the high cyanopolyynes abundance indicates that there may be something special about TMC1 and its neighbour TMC2 which is similar. Certainly one should note that they are some of the nearest molecular clouds ($\sim 100 \text{ pc} \cong 300 \text{ ly}$) and so are some of the more readily studied. It is certainly important to keep in mind that the cyanopolyynes have large dipole moments and simple partition functions and that no other large molecules match them for (radio) visibility. However chains of at least nine and almost certainly more C atoms are clearly there and even taking into account line dilution one would expect a molecule, such as $\text{CH}_3(\text{C}\equiv\text{C})_2\text{C}\equiv\text{N}$, to be more abundant and the spectra (Fig. 6) easier to detect than that of HC_9N , which does not appear to be the case.

Recently C_3N , first detected in IRC+10216 has been found in TMC1 (Friberg *et al.*, 1980). This is an interesting observation and suggests that there may be some close relationship between these two apparently rather different types of object. The possibility that the molecules detected in clouds such as TMC1 could have been produced in a circumstellar shell has been considered but presents problems (Dalgarno and Black, 1976).

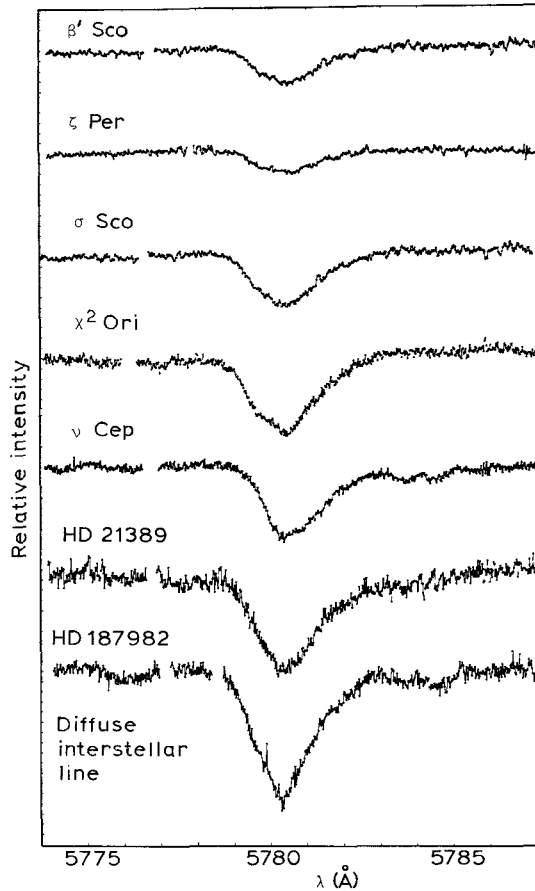


FIG. 37. A set of observations of the diffuse interstellar line at 5780 Å observed against several background stars by Snell and Vanden Bout (1981).

The question is, however, whether the problems with this molecule production mechanism are any more serious than are those that beset grain surface catalysis and gas phase ion-molecule schemes? It is not at all clear that they are.

Giant molecular clouds (GMC)

The tiny 4 ft Columbia University telescope has mapped vast regions of the galaxy in CO (Cohen *et al.*, 1979). Because it is small, it is possible to sample the large areas much more quickly than is feasible with a large telescope, though of course the high spatial resolution information is lost. How important this loss is to the conclusions drawn from low resolution data remains to be seen. Solomon and Sanders (1979) have carried out complementary higher resolution surveys with a larger telescope (Fig. 17). These and other studies have culminated in the result that the inner region of the galaxy is littered with GMC's like those in Orion (Fig. 26). Some 5000 or so appear to be concentrated in a roughly doughnut shaped ring 8–4 kpc in radius about the galactic centre. Their average mass is $\sim 10^6 M_{\odot}$ and their dimensions 100–200 ly. These clouds appear to be the largest and most massive, single, gravitationally-bound objects in the Galaxy. It is not clear how

old these objects are, however they do appear to be at least 10^7 years old (Cohen *et al.*, 1979) and perhaps even older (Solomon and Sanders, 1979; Solomon, Scoville and Sanders, 1980). The Columbia studies indicate that the GMCs congregate mainly in the spiral arms but in the other study this is not so obvious. The surveys indicate that CO is taking over from the H 21 cm line as the major probe of galactic structure. The future task of mapping the Galaxy in CO and determining the relationships between large and small scale studies is the most important in galactic astronomy.

Comets

Similar types of molecule to those observed in the ISM have been detected in comets. The identification by Douglas (1951) of C_3 seems to fit rather neatly with the recent detection of carbon chain molecules. Ions and radicals have been identified and most interestingly so too has the ion H_2O^+ by Wehinger *et al.* (1974). This detection may be an indicator that icy water particles are a major component of the comet's structure. A short recent review of the chemistry of comets has been given by Oppenheimer (1980).

These objects demand further attention because they may well be test tube samples of the ISM brought directly to our doorsteps for analysis. We tend to think of comets as individual objects but it is possible that large clouds of comet-type objects exist which emit radio waves and it could be difficult to show that the cloud has such an inhomogeneous microstructure. Certainly the rôle of comet-size objects in the formation of stars and planets is not understood and it is possible that such objects form at some important phase of cloud collapse.

So far the molecules CH, CH^+ , CN, C_2 , C_3 , CO, CO^+ , CO_2^+ , CS, OH, OH^+ , H_2O^+ , NH, NH_2 , HCN, CH_3CN and N_2^+ have been detected in comets.

INTERSTELLAR CHEMISTRY

Ever since the detection of CH, CH^+ and CN the problem of how such molecules could be formed and survive in the ISM has been a field for study. The detections of OH and the further molecules detected since 1968 (*see* Table 1) have injected the study of interstellar chemistry with a new lease of life. It is not at all clear at this moment that we really understand the problem. New discoveries always seem to chip away at the confidence previously placed in a particular scheme. A general review has been presented by Watson (1976).

There are three main theories each with adherents who cling (like all true believers) with grim attachment to their own particular credo. The three main processes are:

1. Reactions on grain surfaces.
2. 2-Body gas phase ion molecule reactions.
3. Circumstellar shell formation followed by ejection into the ISM.

Of course all three may be important in general and one may be more or less important in one part of the ISM than another. The balance is certainly not at all clear.

In general two colliding atoms (i.e. two H atoms) cannot stick together unless the excess kinetic energy is taken away by a third body. This may be a simultaneously colliding third body, an emitted photon or an electron. The first process is governed by the 3-body collision lifetime

$$\tau_{3b} = \sim 3 \times 10^{23}/n^2 \text{ years} \quad (28)$$

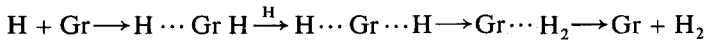
where n is the number density of the ISM, which in the denser regions is mainly H_2 . Even in the denser regions where $n \sim 10^6 \text{ cm}^{-3}$ it takes a bit too long for even one 3-body collision to take place as the Universe is only $\sim 1.5 \times 10^{10}$ years old.

The second process requires a photon to be emitted during a vibrational period ($\sim 10^{-13}$ s). For an allowed infrared transition $\tau_{ir} \sim 10^{-7}$ s and so the lifetime for radiative association is

$$\tau_{ra} \sim 10^9/n \text{ years} \quad (29)$$

The third process is discussed further below.

The big problem is to find a way for H_2 molecules to form in the first place. They cannot form by radiative association as only *quadrupole* emission, which is very weak, is allowed. The most favoured mechanism for forming H_2 is the grain surface catalysed reaction (McCrea and McNally, 1960)



The hydrogen attaches by weak forces to the grain surface at a rate (Watson, 1976)

$$\tau_g \sim 10^9/n \text{ years} \quad (30)$$

after which it tunnels about until it reacts with a second H atom forming H_2 which then detaches. Though H_2 can be detached at low temperatures ~ 10 K it is not clear whether other molecules can get off very easily. CO and N_2 may evaporate but many of the recently detected species such as CH_3CH_2OH or even H_2O might have very great difficulty.

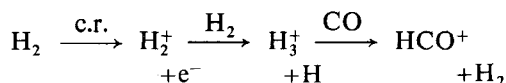
As far as grain chemistry in general is concerned the unknown surface composition is a major problem. Indeed it is fair to say that little if anything is known about their chemical composition. Laboratory investigations which should shed light on this field are being pursued (Hagen, Allamandola and Greenberg, 1979; Greenberg, 1975). It is possible that some chemical mechanisms such as exothermic bond formation may heat up small grains sufficiently for molecules to evaporate or cause localised heating of larger grains. It is also possible that photons and X or cosmic rays or electrons may heat the area where the molecule is attached sufficiently to cause it to unstick.

A large number of possible grain surface reactions have been discussed by Allen and Robinson (1977) as possible routes to interstellar species.

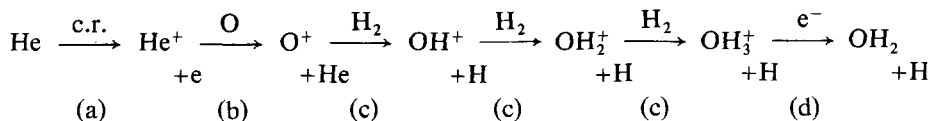
Exothermic gas-phase ion-molecule reactions, many of which have zero activation energies and large reaction cross-sections, offer particularly attractive routes to interstellar molecules. There are several major reviews highlighting various aspects of the chemistry in detail. Solomon and Klemperer (1972), Dalgarno and Black (1976) and Dalgarno (1976) have discussed the chemistry of diffuse clouds, Herbst and Klemperer (1973) that of dense clouds. There are also useful reviews by Huntress (1977), McDaniel *et al.* (1976), Watson (1977, 1978) and in this issue by Smith and Adams (1981).

The ionization of species such as H, H_2 and He by photons in diffuse clouds and cosmic rays in dense clouds is passed on to less abundant atoms such as O, etc, by chains of 2-body transfer reactions which in turn lead to some of the small polyatomic molecules detected in the ISM. Such processes can proceed at the Langevin rate, (Gioumousis and Stevenson, 1958), i.e. at every ion-molecule collision.

A typical example of a chain that can occur in a dense cloud is



for which Herbst and Klemperer (1973) obtain a time to reach steady state abundance $n_{\text{HCO}^+} \sim 10^{-4} \text{ cm}^{-3}$ of $\sim 10^3$ years. There are of course a myriad of similar chains which may be invoked to synthesize other species. For instance H_2O may be formed via a sequence such as



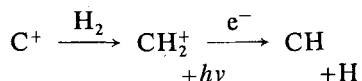
which involves

- (a) cosmic ray ionization
- (b) electron transfer
- (c) three exchange reactions
- (d) a final dissociative e^- /ion recombination.

Clearly the reactions in diffuse clouds are governed by the different overall physical conditions. In the diffuse clouds photons as well as cosmic rays can penetrate and inject the energy which is converted to chemical energy. However, these are relatively unshielded regions and so some form of kinetic balance is set up between the formation and photodissociation processes which allows only the smaller (mainly diatomic) and less readily dissociated species such as CO to survive and build up in significant concentrations.

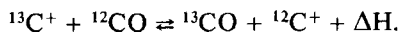
In the denser clouds only high energy cosmic rays can penetrate and inject the requisite energy and once formed the molecules are so well protected by their grain colleagues that they will last indefinitely. It is probably pitch black inside the clouds and pitch may not be a metaphor.

The quantitative studies indicate that the smaller molecules, involving 2–4 atoms can be formed at reasonable rates. Species such as CH may be formed via radiative association steps such as



However the H_2 , needed to form CH , tends to destroy CH^+ (via: $\text{CH}^+ + \text{H}_2 \rightarrow \text{CH}_2^+ + \text{H}$) and so the abundance of CH^+ is still a problem (Dalgarno, 1976). This problem was the first one tackled by Bates and Spitzer (1951) in their pioneering study in interstellar chemistry.

Apart from the fact that many of the small molecules can be accounted for by these processes the observation of HCO^+ , HN_2^+ and HNC are rather convincing indicators that these reactions are significant. In addition the departure of the apparent interstellar isotope ratios from the cosmic ratios seems to be nicely explained by ion-molecule isotope fractionation. Isotope ratios of $\sim 1/40$ for $^{12}\text{CO}/^{13}\text{CO}$ as compared with the terrestrial ratio of $1/89$ have been observed. In the case of D/H as observed in HCN/DCN by Wilson *et al.* (1973) the effect is much larger $\sim 1/100$ as compared with the cosmic value of $\sim 1/10^4$. These effects can be explained by taking into account the exothermicity of exchange reactions such as



ΔH is readily determined from the change in the zero point energy ($^{12}\text{CO} \rightarrow ^{13}\text{CO}$) which is essentially due to the reduced mass dependence of the vibrational frequency. As

$\omega(^{12}\text{CO}) = 2143$ and $\omega(^{13}\text{CO}) = 2095 \text{ cm}^{-1}$. $\therefore \Delta H = 24 \text{ cm}^{-1}$. The equilibrium constant for this process at 80 K has been determined by Smith and Adams (1980) and it fits in beautifully with this simple theory and neatly explains the observed $^{12}\text{CO}/^{13}\text{CO}$ abundances.

The explanation of anomalous isotopic abundances by fractionation is a very strong argument in favour of ion–molecule reactions. These fit nicely as they are fast at the low temperatures as they have negligible activation energies in general. For higher temperature reactions isotope fractionation should be negligible.

Smith and Adams (1977) have determined many of the rate constants required for a detailed analysis of ion–molecule chemistry using the SIFT technique (*see* review in this issue). Huntress (1977) had discussed complementary data obtained using the ICR (ion cyclotron resonance) technique. The effective temperatures of the reactants in the ICR method may be quite high and thus the data may not apply directly to the low temperature ISM.

Prasad and Huntress (1980) have recently presented the results of a very large computer study of the chemistry of the ISM. It is still not at all obvious how molecules such as HC_9N can be produced in cold clouds by a sequence of two-body coupling reactions. Schiff and Bohme (1980) have suggested a possible sequence of steps. It may be that radiative association and neutral–neutral processes may become significantly more important for larger molecules.

The third process which must be taken very seriously is that of molecule formation in high temperature, high density, circumstellar envelopes followed by their subsequent ejection into the general ISM. This mechanism is further discussed in the last section.

DISCUSSION

It would be remarkable if radio spectroscopy were to continue to spring as many exciting surprises in the next decade as it has in the last, but of course this is possible. There are a few areas which can be identified as requiring major efforts in development. New laboratory techniques for producing astrophysically important microwave and infrared spectra are needed. The spectra of free radicals, molecular ions (positive and negative), unstable molecules with multiple bonds and second row atoms are particularly important. More work on high temperature species is also necessary. In addition collisional and radiative energy transfer processes are important and as higher temperature regions are probed, vibrational satellites are becoming detectable. Certainly a great deal of effort is being put into the solution of some of these problems as discussed below.

Obviously one must always strive for higher sensitivity, speed of data collection, spatial resolution, etc. and as successive advances are made some of the goals will hopefully be achieved and new, unexpected discoveries will be made. The most recent high resolution surveys are indicating that the interstellar radio spectrum appears to be rather cluttered up at least at mm wave frequencies. It is now becoming clear that we have only identified the sparse long grass and there may well be a rather dense undergrowth of weak lines which will be difficult to disentangle. Much greater sensitivity may just uncover myriads of weak lines offering few prospects for certain identification. There may thus be a limit to the number of molecules that can be identified by radio techniques ($\sim 150?$).

In the infrared range the problem may be more serious as each vibrational band is accompanied by an entourage of complicated rotational branch structure which will limit the value of the technique for the study of larger molecules.

The study of interstellar molecules is an expanding field, expanding in many directions and the rest of this section is devoted to a review of some of the important questions which

need to be answered and also an attempt to uncover some questions that still need to be asked.

Mapping

In the next phase of this subject a great deal of mapping will probably be carried out and from these some coherent view of interstellar molecule ecology may develop. Certainly this arduous task should form a basis for the determination of the physical conditions which exist in the ISM. The next steps are, of course, to strive for higher and higher spatial resolution by studying higher frequencies such as those in the infrared which in general require higher excitation temperatures or by use of aperture synthesis techniques (Welch *et al.*, 1981). Such developments are extremely important in indicating just how granular the clouds may be. Homogeneity is not an obviously ubiquitous property of the Universe and each successive breakthrough in spatial resolution seems to yield new and unexpected information which requires successive overhauls of the models of interstellar clouds.

There is also room for lower resolution surveys. Just what can be achieved is indicated by the Columbia CO survey using the small 4 ft dish in New York (Cohen *et al.*, 1980; Blitz, 1979; Fig. 26). This survey has shown that molecular filaments link the various clouds (Morris, Montani and Thaddeus, 1980). The survey has also yielded data on the distribution of GMCs in the Galaxy—perhaps some of the most important results as far as astrophysics is concerned—and shown just how extensive the GMCs are with important implications with regard to the structure mass and evolutionary track of the Galaxy.

These studies should yield information about the longevity of the clouds; whether they are 10^7 – 10^8 years old and tied to the spiral arms (Cohen *et al.*, 1980) or even older and concentrated in a doughnut-shaped ring showing no spiral structure (Solomon and Sanders, 1979). As far as astrophysics is concerned a knowledge of molecular distributions will assist the understanding of the energy balance mechanism which controls cloud collapse to star and planet formation. The discovery of molecules showed that clouds could keep cool by losing energy at very low temperatures by rotational emission. The cloud gravitational energy thus converts via kinetic energy to rotational energy and then to microwave or infrared photons which leave the cloud at the velocity of light. In this way a better understanding of the cloud collapse scenario has evolved.

The spatial abundance relationships between molecules should assist in deciding which, if any, of the various chemistries is most important. Searches probably by the new infrared techniques for stars, hot or cold, new or old, embedded in the clouds are also important to this end. It is certainly now clear that maps such as those of Beckwith *et al.* (1978) (Fig. 30) must be the first shots for the baby star scrap book. The more we can learn about the birth of stars the more we should learn about planet formation—something which seems to be only vaguely understood (Hartman, 1978). Indeed this situation should cause us to stop and reflect that even though we have much more detailed information about the solar system than any other bit of the Universe we appear to understand its origin less well than the rest!

Laboratory experiments, theoretical calculations and future radio detections

As the sensitivity of the radio technique improves there will undoubtedly be new molecular identifications and it is perhaps instructive to conjecture what possible new results may turn up.

The recent detections of HNCS (Frerking, Linke and Thaddeus, 1979), CH_3SH (Linke, Frerking and Thaddeus, 1979) the sulphur analogues of hydrogen isocyanate (HNCO) and methanol (CH_3OH) indicate that the good old Mendeleevian principle is still

a valuable guide. Thus, we can draw up a list of a few possible contenders—second row analogues of first row interstellar species.

The species HCN and HNC are, as we have seen, well characterized species and there is every reason to suspect that the phosphorus analogue $\text{HC}\equiv\text{P}$ studied by Tyler (1964) and the silicon analogues HNSi and HSiN whose microwave spectra are not known may be detectable. HCP will be difficult to detect because its dipole moment is only 0.39 Debye as compared with 2.985 Debye for HCN. In addition the cosmic abundance ratio P:N is $\sim 1:270$, implying an intrinsic factor of $\sim 1/16\,000$ between the HCN and HCP intensities. The spectra of the symmetric top molecules PH_3 (Helminger and Gordy, 1969) and $\text{CH}_3\text{C}\equiv\text{P}$ (Kroto, Nixon and Simmons, 1979) are more likely to be detectable contenders as interstellar analogues of NH_3 and $\text{CH}_3\text{C}\equiv\text{N}$ respectively.

Perhaps the most likely phosphorus containing species is cyanophosphaethyne $\text{N}\equiv\text{C}-\text{C}\equiv\text{P}$ which was made and studied for the first time with interstellar observation as a priority (Cooper *et al.*, 1978) (Fig. 11). It is a linear molecule and in general these are more readily detected than other species as discussed previously. It is a very close relative of $\text{HC}\equiv\text{C}-\text{C}\equiv\text{N}$ which is quite abundant in some clouds. It also has a fairly large dipole moment of 3.5 Debye. These factors suggest that its intensity may only be about 1/300 of that of $\text{HC}\equiv\text{C}-\text{C}\equiv\text{N}$ for which ^{13}C isotopes with only slightly higher abundance have been detected. Initial search attempts have proved negative. There is some evidence that phosphorus is depleted in the ISM relative to the cosmic abundance. It is however possible that in sources such as IRC+10216 the depletion is less than in the cold clouds.

Phosphaethyne the phosphorus analogue of $\text{CH}_2=\text{NH}$ (Johnson and Lovas, 1972) was first detected by Hopkinson *et al.* (1976), (Kroto *et al.*, 1980). The species $\text{CH}_2=\text{CHC}\equiv\text{P}$ (Ohno, Kroto and Nixon, 1981) and $\text{HC}\equiv\text{C}-\text{C}\equiv\text{P}$ (Kroto, Ohno and Nixon, 1981) are also known. They are the analogues of $\text{CH}_2=\text{CHC}\equiv\text{N}$ detected by Gardner and Winnewisser (1975) and $\text{HC}\equiv\text{C}-\text{C}\equiv\text{N}$ detected by Turner (1971).

Several sulphur analogues of oxygen compounds have already been detected. The observation of OCS (Jefferts *et al.*, 1971) is a good indication that CO_2 is quite abundant and it can only be a matter of time before it is detected by one of the new infrared techniques. CS is well studied and a radio line from the Orion molecular cloud is shown in Fig. 29 (Scoville, 1979). The widespread abundance of H_2CO (Chaisson, 1978), the detection of acetaldehyde $\text{CH}_3\text{CH}=\text{O}$ (Gottlieb, 1973) and ketene $\text{H}_2\text{C}=\text{C}=\text{O}$ (Turner, 1977) together with the detection of H_2CS (Sinclair *et al.*, 1973) suggest that thioacetaldehyde, $\text{CH}_3\text{CH}=\text{S}$, and thioketene, $\text{CH}_2=\text{C}=\text{S}$, whose microwave spectra are known (Kroto and Landsberg, 1975; Georgiou, Kroto and Landsberg, 1979), should be detectable.

The detection of formic acid, HCOOH by Zuckerman, Ball and Gottlieb (1971) suggests that its thio analogues might be detectable. Monothioformic acid HCOSH has been studied by Hocking and Winnewisser (1977). The recent possible detection of HOCO^+ (Thaddeus, Guélin and Linke, 1981) indicates that it might be worthwhile searching for HOCS^+ and HSCS^+ , etc. Liszt (1978) has discussed searches for magnetic dipole transitions of S_2 .

Silicon analogues are of great interest to chemists as well as astronomers. A significant point about Si is highlighted by Fig. 29 where the spectrum of SiO from Orion is compared with that of CS from the same source. The line widths imply that SiO is only detected in the high temperature expanding cloud in the region of the KLBN source and not in the surrounding cloud presumably because it has condensed out in grains. Some very likely candidates for detection are the species HSiN (Lovas, 1974) and HNSi, analogues of HCN and HNC. Ab initio calculations aimed at estimating the B_0 values of these two species (Kroto *et al.*, 1978) revealed the interesting prediction that the *iso* species HNSi should be much the more thermodynamically stable, the reverse situation exists in the case

of HCN and HNC. These calculations seem to yield B_0 values to ~ 1 per cent. In this case for instance $\Delta E(J = 1 \rightarrow 0) = 2B = 79\,070 \pm 130$ MHz for HNSi. These calculations indicated a similar preference for Si to form $\text{CH}_2=\text{Si}$ rather than $\text{HC}\equiv\text{SiH}$ the acetylenic analogue (Murrell, Kroto and Guest, 1977). The former extremely interesting species was detected by Dubois and Leclercq (1980) by its electronic spectrum using a flash discharge technique during the study of C/Si species of astrophysical interest. This species, which will have a rather similar microwave spectrum to CH_2S , should be detectable in similar regions to those where SiO is observed. Some other interesting Si species are known, at least by their optical spectra such as SiC_2 (Kleman, 1956) and SiH_2 (Dubois, 1968). SiC_2 is one of the Si analogues of C_3 identified by Douglas (1951) as the carrier of the 4050 Å comet bands.

It can only be a matter of time before even longer cyanopolyynes are discovered. The most recent results indicate that the ratio of $\text{HC}_9\text{N}/\text{HC}_7\text{N}$ in TMC1 is $\sim 1/4$ (Broten *et al.*, 1978). This seems at first to be an unusually slow decrease in polyynes abundance with increasing chain length. Interestingly and perhaps importantly $\text{CH}_3\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$ does not appear to be so readily detected as the linear cyanopolyynes. One possible reason is of course the line dilution effect, caused by the third degree of freedom which distributes the available molecules among the various $|K|$ states for a given value of J as discussed previously. The rotational frequencies of the longer systems $\text{CH}_3(\text{C}\equiv\text{C})_2\text{C}\equiv\text{N}$ and $\text{CH}_3(\text{C}\equiv\text{C})_3\text{H}$ are known (Alexander *et al.*, 1978) but so far searches have been unsuccessful. The molecule $\text{CH}_2=\text{CHC}\equiv\text{N}$ has been detected by Winnewisser and Gardner (1975) but its spectrum does not appear to be that strong. This species differs from $\text{HC}\equiv\text{C}-\text{C}\equiv\text{N}$ by the addition of two extra H atoms and its low abundance may be significant as far as the origins of these molecules are concerned. The species $\text{CH}_2=\text{CH}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$ which is related to HC_5N in a similar way has also been made and its microwave spectrum studied (Kroto, Phillips and Walton, 1982). Similarly the molecule $\text{HC}\equiv\text{CNCO}$ related to HNCO (Buhl, Snyder and Edrich, 1972) and the polyynes has also been made and studied (Cooper, Kroto and Walton, 1982).

Herzberg (1980) has discussed the interplay of molecular spectroscopy and astronomy and highlights ways in which future advances may be forthcoming with particular reference to the species HeH^+ , HNe^+ , H_3 , H_3^+ , HC_nN etc.

There a large number of free radicals and unstable molecules whose electronic spectra are known but whose microwave and infrared spectra are only now being studied. Many of these such as C_3 , C_2N , CNC , NCN , CN_2 , N_3 , HNCN , NCO , etc. are quite feasible interstellar species and their known properties are listed by Herzberg (1966).

A wide range of techniques is being developed for the study of the high resolution spectra of molecules which are temperamental in the laboratory (Carrington, 1974, 1980; Morino *et al.*, 1979).

The microwave techniques developed by Woods and coworkers (Woods, 1973; Gudeman *et al.*, 1981) for studying species in discharges have proven extremely valuable in confirming the U line assignments particularly in the case of the molecular ions (*see* page 345). An improvement in the sensitivity of this method would yield some extremely valuable laboratory frequencies for new molecular ions and so guide radio searches. Such an advance would also assist in the assignment of some of the 120 known U-line frequencies (Turner, 1979) some of which are quite likely to belong to slightly more complex and perhaps also more stable molecular ions than the very simple linear ones so far assigned.

Particularly interesting advances in the methods for obtaining spectroscopic data from molecular ion beams using lasers have been developed by various groups including Wing *et al.* (1976) and Carrington and Sarre (1977) to work in the optical and infrared regions. The data obtained at infrared frequencies should pay astrophysical dividends as infrared

astronomy improves. At present there are no sufficiently sensitive microwave techniques to carry out general laboratory searches for new rotational frequencies of ions. A most important breakthrough in ion spectroscopy has been made by Oka (1980) who has observed H_3^+ using a very sensitive tunable infrared laser to detect the very weak absorption directly through a hydrogen gas discharge. The molecule is the first equilateral triangle species detected. The interaction between laboratory infrared spectroscopy and infrared astronomy promises to provide more exciting information in the future especially about protostellar objects.

One of the most valuable advances in high resolution spectroscopy of free radicals is that developed by Evenson and coworkers (*see, for instance, Evenson et al., 1980*). This is the technique of laser magnetic resonance which recently was used to detect C atoms in the laboratory (Saykally and Evenson, 1980). The detection of interstellar C (Phillips *et al., 1980*) was facilitated by this measurement. As far-infrared astronomical sensitivity improves this particular technique should yield as valuable interstellar information as the molecular information already produced.

Theoretical calculations have played a useful rôle in this field, especially in adding to the circumstantial evidence used to identify some of the U lines. In general they have been ab initio calculations on rather simple systems such as HCO^+ , HNC , etc. and it seems that the rotational constants for these systems can be calculated to about 1 per cent. This is really not good enough for certain identification, however it is often useful to rule out possibilities (Kroto *et al., 1978*). In only one case has a calculation been truly successful and that is the special case (Oka, 1978) in which HC_9N was identified by numerical extrapolation (Brotten *et al., 1978*). There are few cases where this procedure is likely to be as successful as in the case of the polyynes (perhaps C_nH and C_nN).

The general value of theoretical calculation has been reviewed by Wilson (1980) who has given references to calculation on such species as: CSiH , SiCH , HSiO^+ , HOSi^+ , HSiN and HNSi , which are likely to give rise to detectable interstellar radio lines.

Grains and chains

It is clear that interstellar molecules are tied to grains and it is unlikely that we shall be entirely sure about molecule formation and the associated cloud \leftrightarrow star transition without a much more concrete understanding of what grains are. Grains have been identified by a process of elimination in that it is not obvious what other medium could give rise to the observed wavelength dependence and polarization characteristics of the interstellar scattering. The lemma to Holmes' Law may apply here in that we have to be certain that all other alternative possibilities have been eliminated before we can be sure the last one that remains is correct. It seems now worth considering how molecules may affect the picture. The long chain molecules may hold a key to some important properties. The detection of cyanopolyynes and their probable coexistence with grains implies that a whole range of C_n chains, where n may become very large, may exist in the ISM. Douglas (1977) has suggested that C_n chains may be responsible for the diffuse interstellar lines. Whether or not they are it seems certain that these chains may be ubiquitous. The interventions of H and N atoms will chop the chains giving them neat ends (i.e. either $\cdots\text{C}\equiv\text{C}-\text{H}$ or $\cdots\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$) and large dipole moments which allow them to be detected by radio techniques. The results suggest very strongly that the species: C_n , C_nH , C_nN , HC_nH and NC_nN (and perhaps C_nO , etc.) must be very abundant and indeed the detection of the cyanopolyynes may only be the tip of the iceberg as they are the only ones which we can at present detect readily. Species such as HC_nN will be rather more difficult to detect in warmer clouds due to the line dilution caused by the excitation of the vibrational degrees of freedom (Fig. 22). Hot molecules flex so much that effectively they are no longer linear

and thus lose the linear advantage by populating the bending vibrational (third rotational) degree of freedom.

Such large molecules may not be so readily photodissociated as the energy of electronic excitation will tend to distribute evenly along the chain rather than concentrate in a particular part of the molecule. At low pressures these chains may be kinetically stable as entropy related geometric factors stabilize them against chemical reaction.

The existence of such species in the ISM may have optical repercussions. Simple free electron theory indicates that they should have large electronic transition coefficients. The bands should leak down to longer and longer wavelengths as the chains increase in length. The effect on the optical transmission of the ISM may well be significant especially if it is realised that resonant and non-resonant (Rayleigh) scattering may be important. The wavelength dependence of the scattering will be a complex convolution due to an ISM filled with a whole range of molecules including a significant proportion of chains.

The polarization of light by passage through the ISM has been explained by scattering due to needle shaped grains aligned by interstellar magnetic fields. It is possible that if significant numbers of even- n C_n chains exist in space they may align because they may be paramagnetic. Although the ground state of C_2 is diamagnetic the $a^3\Pi$ excited state is only 716.24 cm^{-1} higher (Ballik and Ramsay, 1963). The separation between the states is likely to be smaller or even inverted in longer chains and there is thus a possibility of a simple strong mechanism for alignment by interstellar magnetic fields of an interstellar species with optical properties that may significantly affect the interstellar extinction.

There are a few experimental clues that indicate that there is something special about the chemistry of chain molecule formation. For instance it is well known that C_n molecules exist in the vapour over carbon at high temperature and that the proportion of longer chains increases with temperature above 2000 K (Chupka and Inghram, 1955). It would also appear that there is an alternation in the stability as the chains with odd n are more stable than adjacent chains with n even (Pitzer and Clementi, 1959). An observation which at the time was unique was made by Schüler and Reinbeck (1951) who observed the so-called T spectrum emitted from discharges in hydrocarbons. The bands were particularly strong from diacetylene and acetylene discharges. The carrier was positively identified as the ion $\text{HC}\equiv\text{C}-\text{C}\equiv\text{CH}^+$ by Callomon (1956). Recently cyanopolynes have been produced in discharges by Winnewisser *et al.* (1980). It is certainly very likely that such molecules are among the *primary* gaseous species produced in Urey-Miller type experiments and do not survive the secondary reactions that occur, particularly in the condensed phase.

The properties of interstellar grains have been reviewed by Aanestad and Purcell (1973).

The diffuse interstellar lines

As far as the diffuse interstellar lines are concerned it is not at all clear what the right mode of attack might be, if indeed there is one. Certainly even better spectra are needed and efforts in this direction are continually being made.

Thus accurate relative intensities, line widths and frequencies together with higher resolution of the detailed line shapes will be invaluable. With the best data available it may be possible for someone to pick up the crucial lead and solve this 50 year old problem. It is not clear whether laboratory experiments are worthwhile. If the lines belong to absorbers trapped in grain matrices then the problem depends not only on the trapped species but also on the grain material which causes matrix line shifts. It is of course possible that the lines belong to some extremely weak optical resonances of grains or free molecules which only become detectable at colossal path length which would be impossible to emulate in a terrestrial laboratory.

Chemistry

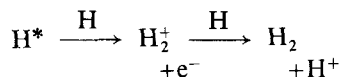
The significance of the clear evidence that objects such as IRC+10216 are pumping molecules, and probably grains as well, into the ISM needs to be clarified. Such objects have only become detectable with the improvement of infrared techniques and it is important to determine how widespread they are and whether they can account for the huge quantities of molecules observed.

There are several arguments to suggest that circumstellar shell formation is not of primary importance (Dalgarno and Black, 1976). At present there do not seem to be enough stars around pumping out enough material. In addition the lifetime of an average unshielded molecule is ~ 1000 years and this is not long enough for molecules to survive the journey to the cold regions where they are seen.

The exciting discovery of a wide range of typical interstellar molecules in cool stars such as IRC+10216 suggests that these arguments should not go unquestioned.

The significant amounts of carbon, oxygen and nitrogen must have been formed in stars and so there must have been enough of them around at some time to form the amount observed. One fairly well accepted mechanism is that grains are formed in circumstellar shells and it now appears that molecules form at roughly the same time. Having been formed simultaneously they may take part in a symbiotic protection-formation cycle during various stages of molecular cloud evolution. The scenario that follows from this is one in which the interplay of radiation induced gas-phase reactions and grain-surface catalysis are secondary processes rather than the primary formation route.

A curious inconsistency in the presently accepted chemical schemes is the fact that the only viable mechanism for the formation of H_2 , the most important molecule of all, is via grain-surface catalysis (McCrea and McNally, 1960; Hollenbach and Salpeter, 1971) and yet for *all* other molecules, gas-phase processes are invoked. It is possible that in some regions, such as a secondary halo outside the HII region, a process such as



might occur as all excited H atoms with $n \geq 3$ have enough energy to form H_2^+ . Indeed the detection of atoms with $n \sim 100-300$ indicates atom diameters of $\sim 1/100$ mm† implying colossal cross-sections and perhaps not insignificant lifetimes for the H^* atoms to filter down below the $n = 3$ level.

Radiative association processes are at present being invoked as possible mechanisms for the formation of large molecules. It is likely that the more complex conditions that occur during collisions in larger molecules should allow the collision complexes longer time to dissipate excess kinetic energy, initially throughout the molecule, and then via the many more accessible molecular emission routes. It may in the future be possible to study these types of process directly. Smith and Adams (1981) have obtained circumstantial data on these types of processes.

Other molecule formation scenarios

One question of importance to interstellar chemistry relates to the efficiency with which stars and planets form. These processes are thought to be very inefficient and if so, one really needs to know just how inefficient they are and in what form the waste material is

† $a_n = 0.529n^2 \text{ \AA} \therefore \sim a_{300} \sim 10^5 \text{ \AA} \sim 10^{-2} \text{ mm}$ where a_n is the n th Bohr orbit.

left. There most certainly will be molecules formed by a sort of *Damp Squib Mechanism* of interstellar molecule formation.

There are many other ways in which the ISM may be coerced into forming molecules. An interesting possibility is that they may form along accretion wakes caused by the passage of stars or star clusters through the ISM. Stars may be able to create the required density/temperature conditions for these reactions to proceed efficiently in interstellar clouds and leave a trail of molecules in their wake.

At the end of this review one might ask 'what, if anything, have all these recent discoveries got to do with the question of Life, the Universe and Everything that the mice wished to understand' (Adams, 1979)? Well, although we are still having to think about it, there is at least one curious observation that can be made about bio-emotive molecules such as glycine. It now seems certain that such molecules are formed in circumstellar shells and ejected into the ISM. A presently accepted view is that these molecules are then destroyed and gas phase or grain surface processes produce them a *second* time in the centres of cold, dense clouds. The planetary specialists suggest that they are then destroyed yet again during planet formation where they are synthesized for a *third* time in the earth's prebiotic secondary atmosphere via Urey-Miller type processes (Keosian, 1968). Why should these molecules be made three times? Can we be quite sure that the molecules are destroyed and in particular is it possible that the molecules can indeed survive either one or both the processes of star cloud migration and planet formation?

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