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 (Cleeton 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 discus-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 $n_H \sim 10^{-1}$–10^{-2} cm^{-3} to an average density of 1–10 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 ≡ 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.

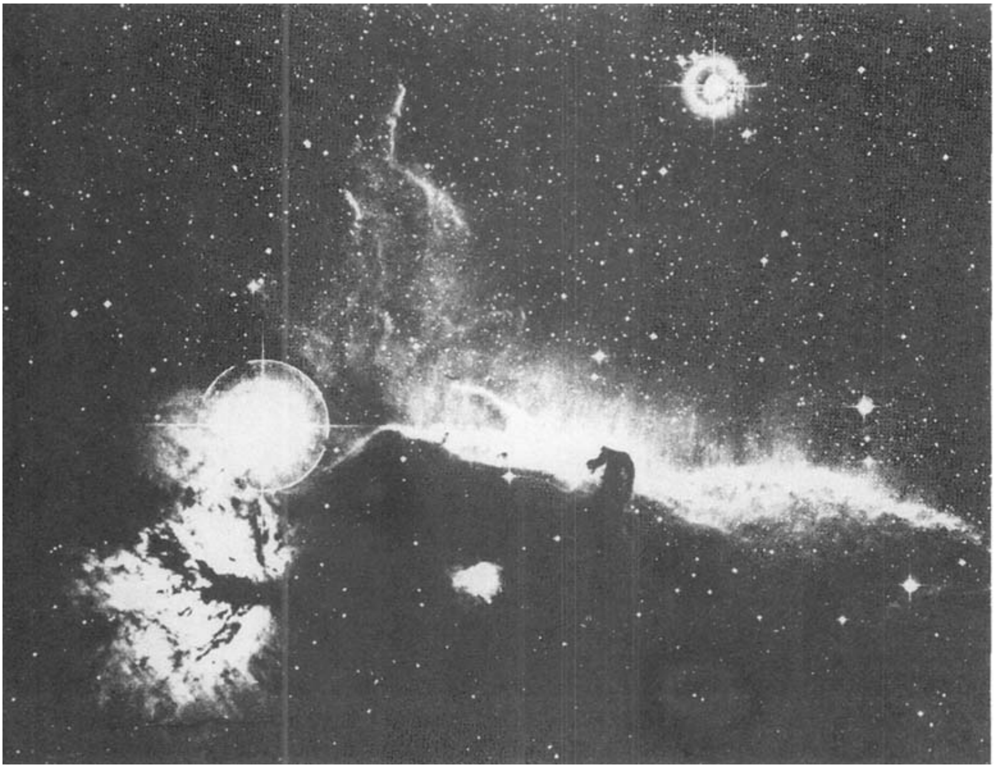

FIG. 2. The bright emission nebula IC434 silhouetting the Horsehead dark cloud in Orion (taken from Murdin, Allen and Malin 1979 UKSTU). Compare this picture with the map in Fig. 26. NGC2024 lies just to the NE of ζ Orionis the easternmost star in the belt of Orion. IC434 glows due to photoionization 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 $\sim$ 10–100 $M_\odot$, size $\sim$ 1–3 ly and $n \sim$ 1–10 cm^{-3} (mainly H_2). There are larger inhomogeneous clouds often associated with stars and sometimes called molecular clouds where $T \sim$ 25–50 K and $n \sim 10^4$–$10^5\,\text{cm}^{-3}$ 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 $\sim 10^5$–$2.5 \times 10^6\,M_\odot$ 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 $|n\rangle \leftrightarrow |m\rangle$ can take place either spontaneously or under the influence of a perturbation by radiation or a collision with another molecule or atom.