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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 NH_3, CO and H_2O (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 H_2 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 (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.