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Excerpt
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1

A brief history

I have suspected that history, real history, is more modest and that its essential dates may be, for a long time, secret.

Jorge Luis Borges in 'The Modesty of History' in *Other Inquisitions, 1937–1952*

1 A brief history

The field of molecular astrophysics has grown to be a vital one through the efforts of a large number of dedicated researchers, many of whom had distinguished careers in other disciplines before pursuing the topics treated in this volume. A full history of the development of molecular astrophysics would require another book with thousands of references to works published over nearly seven decades. Here we present a very broad sketch of the evolution of the subject and emphasize the rapid observational and theoretical progress that has occurred in the last twenty years and will continue, in part due to the availability of new observing technologies, well into the next century.

1.1 The dawn of the field

In 1926 the 44 year old Sir Arthur S Eddington was invited to deliver the Royal Society's Bakerian Lecture. He was already world famous for having led the first expedition to test Einstein's general theory of relativity by measuring, during a solar eclipse, the apparent shifts (induced by the Sun's gravity) of stars with lines of sight near the eclipsed Sun's rim. In addition, Eddington had made and was to continue for two more decades to make penetrating contributions on which much of modern astrophysics is founded.

The title of Eddington's Bakerian Lecture was 'Diffuse Matter in Space'. This matter consists mostly of the interstellar gas which comprises roughly 1 per cent of the Galaxy's total mass. An additional component of the diffuse matter was recognized to be dust which in many directions obscures all but the nearest stars. The dust was known by Eddington and his contemporaries to be clumped into clouds in which most of the interstellar gas is concentrated. The masses of these clouds are now known to be up to a million times that of the Sun, so that the largest clouds are the most massive objects in the Galaxy. They are also the sites of current stellar birth.

One question addressed by Eddington in his 1926 lecture concerned whether any of these clouds, many of which are very opaque to optical light and which are typically 10^{16} times[†] less dense than the Earth's atmosphere, could contain molecules. Eddington concluded that no processes were known that could form molecules in these clouds at sufficient rates to keep their abundances high.

Yet somewhat more than a decade later, in 1937, T Dunham in the *Publications of the Astronomical Society of the Pacific*, and P Swings and L Rosenfeld in the *Astrophysical Journal*, reported their discoveries of absorption lines attributed to intervening molecules in the optical spectra of bright stars. The molecules were identified as CH, CN, and CH^+. Perhaps the most surprising aspect of the discoveries was that these molecules were detected in clouds that filter out only a moderate fraction of the optical starlight that impinges on them. This

[†] Here, 10^n means a 1 followed by n zeros. Thus, $10^2 = 100$, $10^3 = 1000$, etc. Hence, $10^{16} = 10 \times 10^6 \times 10^9$, or 10 million billion.

contrasts with Eddington's conclusion that even the darkest of the interstellar clouds would contain no molecules.

Attempts were made in the 1940s and 1950s to understand theoretically the origins of the observed molecules, but only in the 1960s were the processes that determine the abundance of molecular hydrogen, H_2, the most prevalent astronomical molecule, identified and studied quantitatively. The theoretical framework in which explanations of the abundances of CH, CN, and CH^+ and many other astronomical molecules are founded was developed in the 1970s, nearly a half century after Eddington's Bakerian Lecture was delivered. Even now (1995), the origin of CH^+ remains controversial. The field of molecular astrophysics has had its successes, as described in this volume, but many interesting problems continue to challenge researchers.

Table 1.1. *Molecules detected in interstellar and circumstellar regions.*

In fact, since many of these molecules have also been detected with the major isotope (e.g. the most abundant form of carbon atom has a mass of 12 atomic mass units and is denoted ^{12}C) substituted by a minor isotope (e.g. ^{13}C), the actual number of detected molecular species is much larger than shown in the list below. For example, CO has been detected in interstellar clouds with all possible combinations of ^{12}C and ^{13}C, and ^{16}O (the main isotope of oxygen) and ^{17}O and ^{18}O (the minor isotopes of oxygen). As another example, in cyanoacetylene, HC_3N, a linear molecule, the ^{13}C isotope can be found in any of the three positions for carbon. The hydrogen atoms in these molecules may also be substituted by deuterium (or heavy hydrogen, ^2H or D). The 'l' and 'c' forms of certain molecules, e.g. C_3H, refer to linear and cyclic geometries.

No. of atoms						
2	3	4	5	6	7	≥8
H_2	H_2O	NH_3	HC_3N	CH_3OH	HC_5N	CH_3OCHO
OH	H_2S	H_3O^+	C_4H	CH_3CN	CH_3CCH	CH_3C_3N
SO	SO_2	H_2CO	CH_2NH	CH_3SH	CH_3NH_2	HC_7N
SiO	NH_2	HNCO	CH_2CO	NH_2CHO	CH_3CHO	CH_3OCH_3
SiS	N_2H^+	H_2CS	NH_2CN	CH_3NC	CH_2CHCN	CH_3CH_2OH
NO	HNO	HNCS	HOCHO	HC_2CHO	C_6H	CH_3CH_2CN
NS	HCN	C_3N	c-C_3H_2	H_2C_4		CH_3C_4H
HCl	HNC	c-C_3H	CH_2CN	C_2H_4		HC_9N
PN	C_2H	l-C_3H	H_2C_3	$H_2C_3N^+$		$HC_{11}N$
NH	HCO	C_3S	CH_4			CH_3C_5N
CH^+	HCO^+	C_3O	HC_2NC			$(CH_3)_2CO$
CH	OCS	C_2H_2	SiH_4			
CN	HCS^+	$HOCO^+$				
CO	C_2S	$HCNH^+$				
CS	C_2O					
C_2	NaCN					
CO^+	c-SiC_2					
SO^+	MgNC					
SiN						
NaCl						
KCl						
AlF						

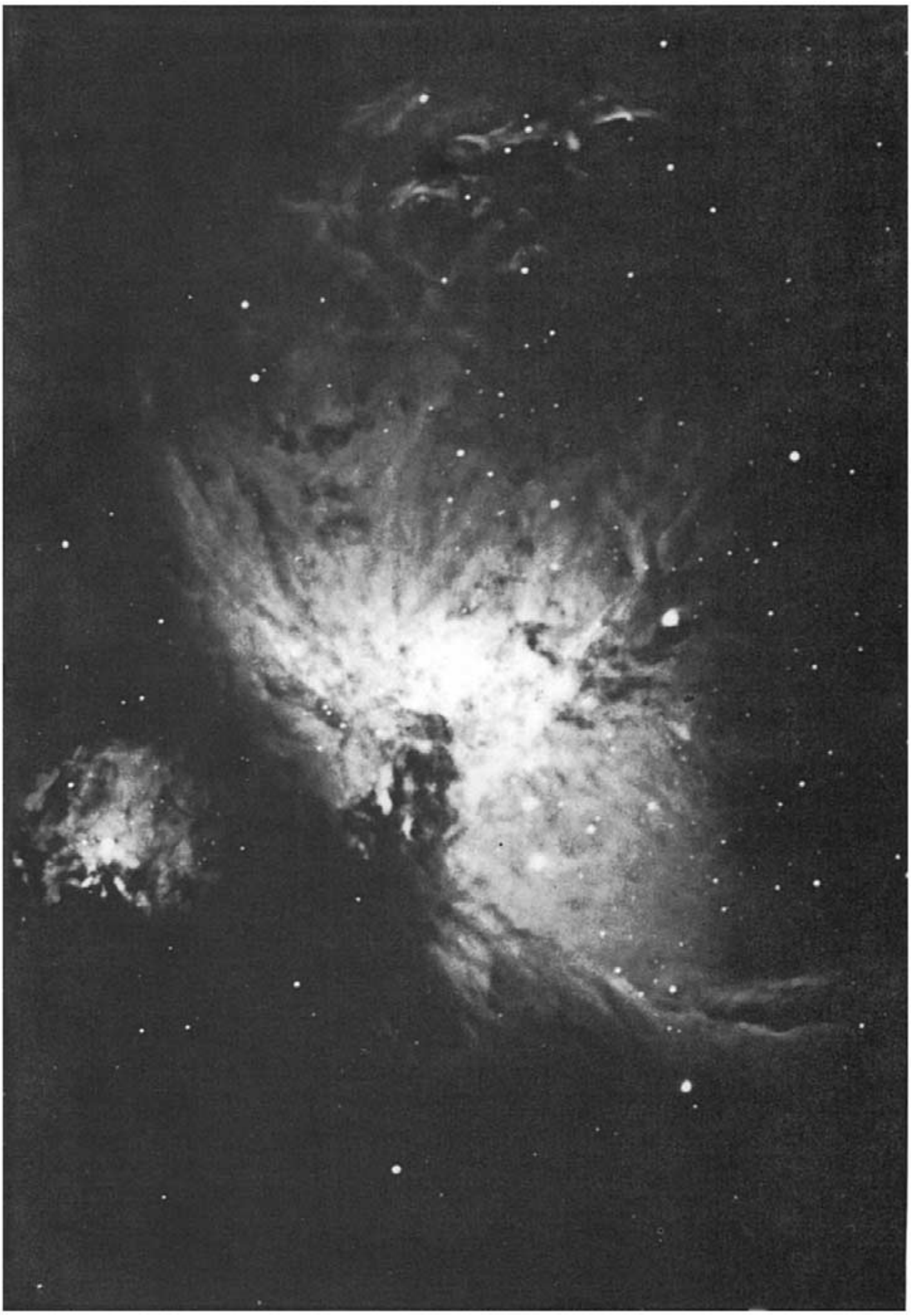

Fig. 1.1. The Orion Nebula (copyright 1981 AAT Board).

1.2 New windows on the molecular composition of the cosmos

The 1960s and 1970s were an era of great theoretical development in molecular astrophysics. However, no scientific area expands in the absence of data; one of

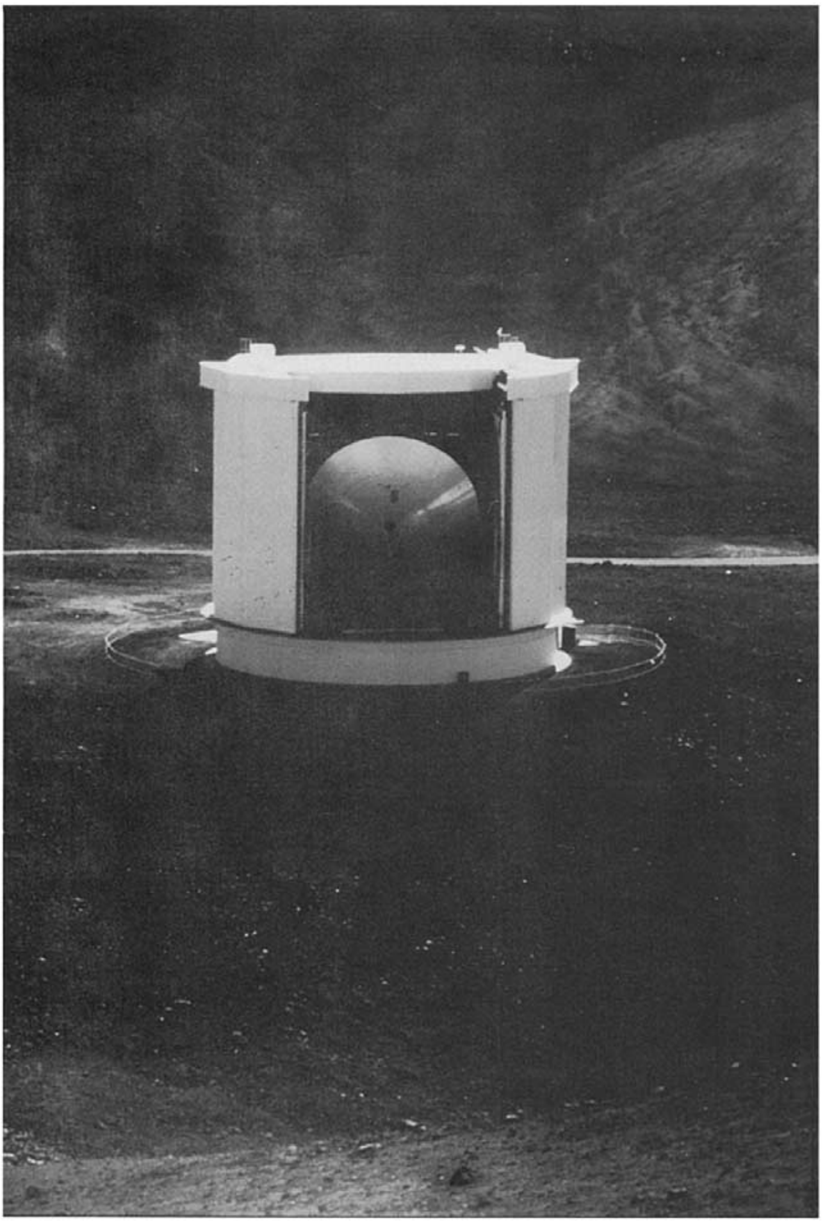

Fig. 1.2. The James Clerk Maxwell Telescope. The JCMT, which is located on a mountain in Hawaii and operated by the UK's Particle Physics and Astronomy Research Council on behalf of a British–Canadian–Dutch consortium, is one of several submillimetre telescopes which permit investigations of molecular emission in a previously unaccessed wavelength range. (Photograph courtesy of Dr A I Harris.)

the major reasons for the theoretical advances of the 1960s and 1970s was the concurrent (and often somewhat earlier) appearances of new methods for observing astronomical sources.

A huge boost to molecular astrophysics occurred with the first radio wavelength detection of an astronomical molecule. In 1963 a detection was made of several spectral features, at wavelengths of about 18 cm, due to absorption by foreground OH molecules of radiation emitted by a remnant caused by the interaction of an exploded star (a supernova) and the interstellar gas around it. As well as absorbing radiation, OH molecules were also observed in emission. In some places OH molecules were found to radiate with roughly ten thousand million (ten billion) times the intensity that was expected. The tremendous strengths of these OH emissions were recognized in the mid-1960s to be due to the action of processes very similar to those operating in lasers, then only recently invented in the laboratory.

Many molecules have rich spectra at wavelengths of a fraction of a millimetre up to tens of centimetres. Radio astronomy's original contributions came from studies at wavelengths of several centimetres to tens of centimetres, but during the 1970s millimetre wave astronomy began to flourish as receivers and dishes designed to work at shorter wavelengths became available. Many tens of molecular species were detected in astronomical sources for the first time in the 1960s and 1970s. The list of astronomical molecules observed at radio centimetre and millimetre wavelengths includes simple molecules like CO (carbon monoxide) as well as complicated ones such as CH_3SH (methyl mercaptan) and $HC_{11}N$ (cyano-decapenta-yne). A list of molecular species that have been detected in interstellar and circumstellar regions is given in Table 1.1.

H_2, in part because of its lightness compared to other molecules and because of its symmetry, does not have a rich spectrum at centimetre and millimetre wavelengths. Many of its lowest energy transitions lie in a range of infrared wavelengths† at which the Earth's atmosphere is opaque, while its highest energy transitions lie at ultraviolet wavelengths‡ at which atmospheric absorption is also a problem. Since hydrogen is the most abundant element, being about ten and a thousand times more prevalent than helium and oxygen (the next most abundant elements), respectively, astronomers anticipated that far more H_2 than any other molecule would exist in most astronomical sources. Even before it was observed, a detailed, quantitative theory for the production and destruction of astronomical H_2 was developed in the 1960s. Then in 1970 H_2 outside the Solar System was detected for the first time. An ultraviolet spectrograph was launched above the atmosphere on a rocket, and absorption due to interstellar H_2 of ultraviolet emission from nearby bright stars was measured. In 1973 the highly successful operation of the *Copernicus* satellite which carried an ultraviolet spectrometer made possible revolutionary studies of interstellar molecular clouds, as well as nonmolecular sources including the

† The infrared region of the spectrum is generally considered to extend from wavelengths of about 1 micrometre (or one millionth of a metre) to hundreds of micrometres. The features of longest wavelength in the spectrum of molecular hydrogen occur around 20 micrometres.

‡ The ultraviolet region of the spectrum extends from wavelengths of about 0.3 micrometres to 0.01 micrometres. The shortest wavelengths associated with molecular hydrogen are around 0.1 micrometres which may also be written 100 nanometres (i.e. 100 nm, the prefix 'nano' meaning division by 10^9).

hot interstellar gas (with a temperature of about one million kelvins) and the atmospheres and winds of the brightest ultraviolet emitting stars.

In 1976 infrared emission from astronomical H_2 was observed for the first time. Special infrared detectors were used on a ground based optical telescope to search at wavelengths around 2 micrometres, one of the narrow infrared bands at which the Earth's atmosphere is not too opaque. Radiation was seen from moderately excited states of H_2 populated in the warm gas (with a temperature of several thousands of kelvins) in the vicinity of young stars in the Orion Molecular Cloud near the Orion Nebula which is pictured in Fig. 1.1.

In the next few years, spectroscopic satellites will permit the study of infrared emission and absorption by many other molecules. In the early 1990s, the use of precisely formed large metallic dishes with diameters of 10–15 m and of special spectroscopic receivers have made possible the study of molecular spectral features at wavelengths of several tenths of a millimetre. The James Clerk Maxwell Telescope, one of those new submillimetre instruments, is shown in Fig. 1.2. Its surface is thinly plated in aluminium, a necessary part of the design to allow the maintenance of sufficient smoothness to work at these short wavelengths. Also, arrays of dishes that operate together to map at high angular resolution sources of molecular emissions in the millimetre wavelength range have become available, and are steadily collecting data for star forming regions and other types of sources. Exciting new discoveries are anticipated from this developing technology.

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2

Setting the astronomical scene

> Man has been here 32 000 years. That it took a hundred million years[†] to prepare the world for him is proof that is what it was done for. I suppose it is. I dunno. If the Eiffel Tower were now representing the world's age, the skin of paint on the pinnacle knob at its summit would represents man's share of that age; and anybody would perceive that the skin was what the tower was built for. I reckon they would, I dunno.
>
> Mark Twain in 'Was the World Made for Man' in 'The Damned Human Race' in the collection *Letters from the Earth*

Our most immediate impression of the world around us is one of stability. In our literature, the mountains symbolize strength and permanence; the seas eternity. The Sun and stars seem immutable, fixed since Creation. Of course, we know that this apparent constancy is illusory. The Universe is continually evolving. The human attention span is so brief that nothing changes significantly in the lifetime of an individual, except for minor local changes, and – occasionally – the explosion of an evolved star in a supernova.

But the evidence of variation can always be found. Even on the Earth, the signs of changes in the atmosphere induced by a mere century of technological activity are there to be read. We know that the changes themselves will not be significant for some decades to come. But the evidence is there, although not immediately apparent. So it is with astronomy. On a casual inspection the Universe may appear unchanging, but the manifestations of development, i.e. of evolution, are there to be interpreted. In this book we are particularly concerned with the evidence provided by chemistry. We shall see that radiation from the molecular products of chemistry generally allows us to probe the cooler and denser regions of the Universe, which may be optically inaccessible. The study of molecules, usually through spectral lines in the infrared and radio regions, therefore complements traditional optical investigations and gives a new perspective.

[†] Current estimates are around 4500 million years, but the ratio of the estimates of the age of the human species and the Earth's age have remained approximately constant since Twain wrote.

Table 2.1. *Ages and lifetimes, in years and in 'A-units' where 10^6 y is 1 'A-day'.*

Age of the Universe	15×10^9 y	41 A-years
Age of the Galaxy	12×10^9 y	33 A-years
Age of the Sun	5×10^9 y	14 A-years
Age of the Earth	4.5×10^9 y	12 A-years
Rotation period of the Galaxy	10^8 y	3 A-months
Life of a molecular cloud	10^8 y	3 A-months
Life of a bright star	10^6 y	1 A-day
Duration of a cool envelope	10^4 y	14 A-minutes
Duration of a planetary nebula	10^4 y	14 A-minutes
Duration of human civilization	5×10^3 y	7 A-minutes
Duration of human technological era	10^2 y	9 A-seconds
Duration of a supernova	1 y	0.1 A-seconds

We shall also discover that chemistry not only allows us to trace the presence of matter in the Universe, but that it actually *controls* the evolution on all scales throughout the Universe. Were it not for the consequences of chemistry occurring at crucial times in the development of the Universe, it would certainly not be as we find it today.

2.1 Timescales

There are two kinds of timescale with which we must be concerned. One is the timescale of events in astronomy; the other is the timescale of events in the chemistry of astronomy. Both these timescales are quite different from our terrestrial experience.

The age of the Universe, i.e. the time elapsed since the Big Bang, is some 15 billion years (we use 1 billion $= 10^9$). The Sun is 5 billion years old, and the Earth is slightly younger at 4.5 billion years. The Galaxy, of which the Sun and its family of planets are members, rotates once every 100 million years. The Sun is evidently long lived. More massive stars burn much more brightly, and though they have more fuel, the largest can only last about a million years.

'Only a million years' – of course, that is an enormous, incomprehensible period of time by human standards. It is the length of time that humanoid beings have been present on Earth; however, human civilizations have been active on this planet only for the last few thousand years. A million years is, nevertheless, a useful period of time in considering astronomical and geological terms. Many processes within the Galaxy occur on this kind of timescale. Let us, therefore, regard a million years as a period of one '*astronomical day*', an '*A-day*', and relate ages and periods of some astronomical events to this new scale of time. Table 2.1 gives the times in years and in A-units associated with some astronomical and historical events. This helps to put timescales into a reasonable perspective.

The table suggests that the Universe is 41 A-years old, while – at the other extreme – human activities have been so recent as to be almost insignificant.

In astronomical terms, bright stars come and go like flowers that bloom for an A-day or two, while each of the 'plants' that produce them – the molecular clouds – remains in being for a season of several A-months. Low-mass stars, like the Sun, are much more common and much more durable. Like the grass in the garden lawn, they can survive for A-decades. The spectacular events that occur in the lives of some stars: a supernova explosion, the development of extensive cool envelopes, the blossoming of a planetary nebula, are really very brief phenomena indeed. Like dandelion seeds carried off by a puff of wind into the garden, these events are soon over.

The chemical timescales are also very important. For two species, atoms or molecules, A and B, to react together and make products requires – as a minimum condition – that the species come into reasonably close contact. If we say that 0.3 nanometres is reasonably close and that most species move with speeds around a few hundred metres per second then the time for a particular species A to be in collision with any of species B is about $10^{16}/n(B)$ seconds, where n(B) is the number of species B per cubic metre. In the Earth's atmosphere, the abundant species such as molecular nitrogen and molecular oxygen have number densities on the order of 10^{25} per cubic metre (m^{-3}), so the time between collisions of these species is really very short, about 10^{-9} seconds, a billionth of a second. However, in the Universe at large the terrestrial conditions are so unusual as to be freakish. We shall see in later chapters (see also Section 2.3) that number densities of the most abundant species, hydrogen, may range from, say, $10^3\ m^{-3}$ in protogalaxies to $10^{20}\ m^{-3}$ in the disks of protostellar nebulae. The range of collisional timescales is, consequently, also very wide. At the lowest densities, collisions of one hydrogen atom with another occur on the average at intervals of 10^{13} seconds, nearly a million years. (A useful approximate conversion is 1 year equals 30 million seconds.) Collisions with other elements are much rarer than this.

Only a fraction of collisions usually leads to reaction of the partners and formation of the products, so at low densities nothing of chemical importance can happen until very long times have elapsed. In stellar atmospheres, however, each molecule may be subjected to hundreds of collisions per second, and chemistry can be rapid.

However, much of the chemistry in astronomy occurs slowly, and local physical conditions (e.g. temperature, density) may change faster so that the chemistry can never 'catch up'. For example, the conversion of atomic hydrogen to molecular hydrogen

$$2H \rightarrow H_2$$

is generally rather slow. A cloud of gas in which much of the hydrogen is still atomic may collapse under its own weight so quickly that even when its density has increased to a value at which one would expect much of the hydrogen to be molecular, the chemistry may not keep pace, and the content of atomic hydrogen may be greater than expected. On the other hand, if the chemistry is very fast, as in stellar atmospheres, then even if the local physical conditions