1
Introduction

1.1 Why Are Molecules Important in Astronomy?

Molecules pervade the cooler, denser parts of the Universe. As a useful rule of thumb, cosmic gases at temperatures of less than a few thousand K and with number densities greater than one hydrogen atom per cm^3 are likely to contain some molecules; even the Sun's atmosphere is very slightly molecular in sunspots (where the temperature – at about 3200 K – is lower than the average surface temperature). However, if the gas kinetic temperatures are much lower, say about 100 K or less, and gas number densities much higher, say more than about 1000 hydrogen atoms per cm^3, the gas will usually be almost entirely molecular. The Giant Molecular Clouds (GMCs) in the Milky Way and in other spiral galaxies are clear examples of regions that are almost entirely molecular. The denser, cooler components of cosmic gas, such as the GMCs in the Milky Way Galaxy, contain a significant fraction of the nonstellar baryonic matter in the Galaxy. Counterparts of the GMCs in the Milky Way are found in nearby spiral galaxies (see Figure 1.1). Although molecular regions are generally relatively small in volume compared to hot gas in structures such as galactic jets or extended regions of very hot X-ray–emitting gas in interstellar space, their much higher density offsets that disparity, and so compact dense objects may be more massive than large tenuous regions.

Such dense, cool regions are of course important in themselves, in adding to our description of the total content of galaxies. But they are also important for our understanding of how galaxies evolve because this denser, cooler gas is the only reservoir of matter for future star formation. Measuring the mass of this reservoir gas in a galaxy and comparing with the existing stellar mass may, for example, give some indication of the evolutionary state of that galaxy. Alternatively, the interaction of an outflow from an active galactic nucleus with cool dense gas in the galaxy can produce a signature chemistry that through

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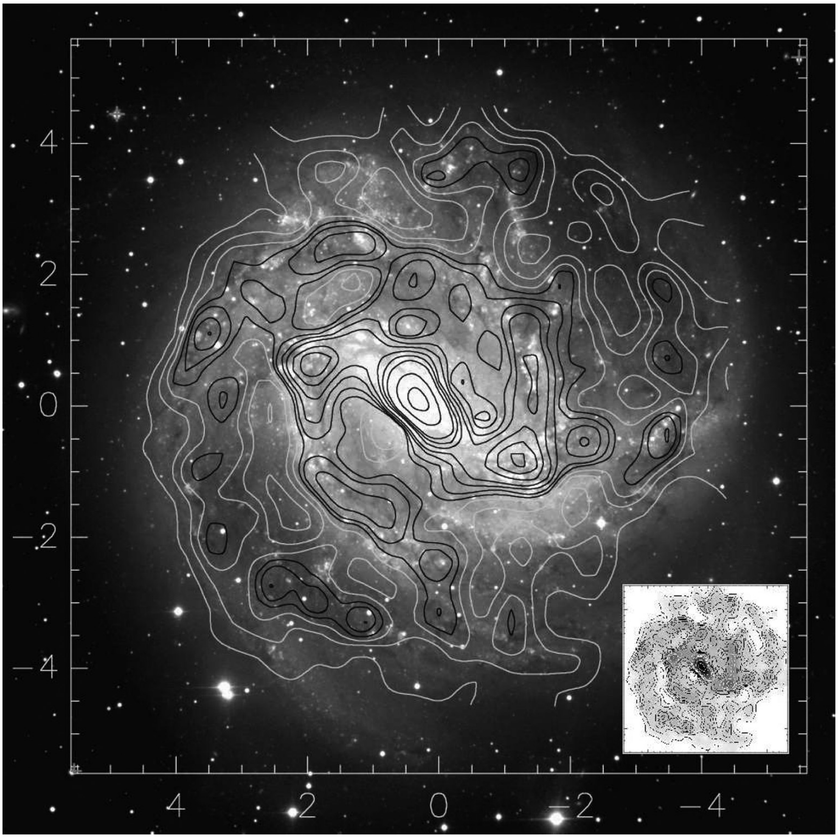

Figure 1.1. Velocity-integrated CO ($J = 1-0$) intensity as contours superposed on a map centre of M83 produced from images in B, V, and R of M83, a nearby spiral galaxy with an estimated mass of 10^{10} $M_\odot$. The x- and y-axes are offsets in RA and Dec from the centre of M83, measured in arcminutes. The average density in the GMCs is of the order of 100–400 cm^{-3}. The CO is associated with small regions of higher densities ($\leq 10^3$–10^5 cm^{-3}) and temperatures of the order of 50 K, where star formation occurs. The inset shows the CO (1–0) map in grayscale. (Reproduced with permission from Lundgren, A. A., Wiklind, T., Olofsson, H., and Rydbeck, G. 2004. *Astronomy & Astrophysics* 413, 505.) Copyright ESO.

its specific molecular emissions may reveal important details of the outflow, such as its mass loss rate. No less important, but on a smaller spatial scale than GMCs, the collapse of gas from a tenuous state to a dense star-forming core can be followed by measuring line emissions from the molecular gas, even though the temperature may be as low as 10 K or even less. Indeed, the low temperature is maintained during much of the collapse by these molecular emissions and also by continuum emissions of the dust. At the end of that collapse process, the newly formed star irradiates any surrounding debris that was not incorporated into the star and generates a new chemistry that provides new molecular signatures. In particular, a protoplanetary disk surrounding the young star is the location in which planet formation occurs, and is also almost entirely molecular. The disk responds to the intense and growing radiation from the central star, and to its powerful wind, in processes that can generate new and useful diagnostic molecules.

Thus, many processes of topical interest in modern astronomy and astrophysics involve cold dense gas or the interaction of radiation or of violent processes with cold dense gas. This book is offered as a guide for astronomers who wish to use molecules as probes of these kinds of processes, and in particular to address the following main questions:

- What kinds of molecules arise in different astronomical situations?
- Which molecular species are the most useful tracers of gas in these different situations?
- Which molecular species are the most useful for determining important physical parameters (e.g., cosmic ray flux, local radiation field, elemental abundances, and so forth) in those situations?
- How does one convert basic observational data taken at the telescope to astrophysically useful information (e.g., column densities or fractional abundances) about an astronomical object?

1.2 A Very Brief History of the Discovery of Molecules in Space

Optical absorption lines, apparently molecular in origin, were first detected in 1937 in the spectra of bright stars, along lines of sight through the diffuse interstellar medium of the Milky Way. A few years later, on the basis of laboratory work, these and other lines were attributed to the diatomic radicals CH, CH^+, and CN. No further detections were made until 1963, when OH masers were detected in the radio. Advances in detector technology permitted the development of millimetre wave and submillimetre wave astronomy and led to a veritable flood of new detections of molecular rotational transitions beginning in 1967. Some detections in other parts of the electromagnetic spectrum were also important. Molecular hydrogen, which has no dipole and therefore very weak rotational transitions, was first detected by a UV rocket experiment in 1970 by absorption in the Lyman and Werner bands; see Figure 1.2 for a

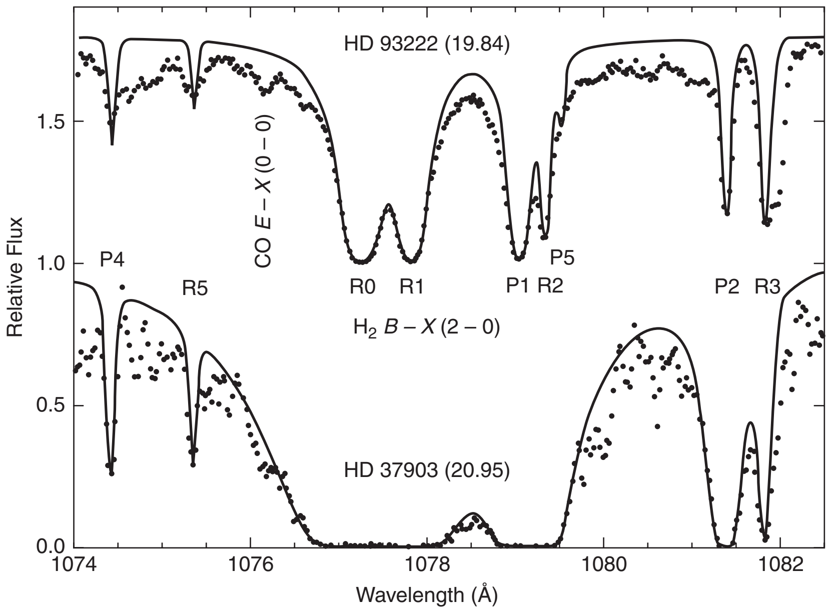

Figure 1.2. A piece of the UV absorption spectrum of H_2 towards two diffuse lines of sight taken with the space observatory Far Ultraviolet Spectroscopic Explorer (FUSE). These spectra show the electronic as well as ro-vibrational structure of the fundamental molecule H_2. The solid lines represent model fits to the spectra. The main features are the B–X (2–0) vibrational bands, and are labelled in the conventional notation (see Chapter 2). Here X represents the ground electronic state and B the first stable excited electronic state. The logarithm of the total hydrogen column density is indicated for each line of sight. (Reproduced by permission of the AAS from Sheffer, Y., Rogers, M., Federman, S. R., Abel, N. P., Gredel, R., Lambert, D. L., and Shaw, G. 2008. *Astrophysical Journal*, 687, 1075.)

recent detection. Molecular hydrogen is the seminal molecule for all interstellar chemistry, as we shall see.

From that time, the number of detected molecular species rose rapidly year by year and it soon became clear that the interstellar medium is a chemically complex environment (see e.g., Figure 1.3). An up-to-date list of detected molecular species is maintained at several websites (e.g., http://www.astro.uni-koeln.de/cdms/molecules/). A list of detected molecular species (as of 2012) organised by type of source is provided in Table 1.1.

Many isotopic varieties, in which, for example, D replaces H, or ^{13}C replaces ^{12}C, or ^{17}O or ^{18}O replaces ^{16}O, are also found, so that the total number of identified molecular species in interstellar and circumstellar space is very much larger than the total of main isotopes (which is currently $\sim$180).

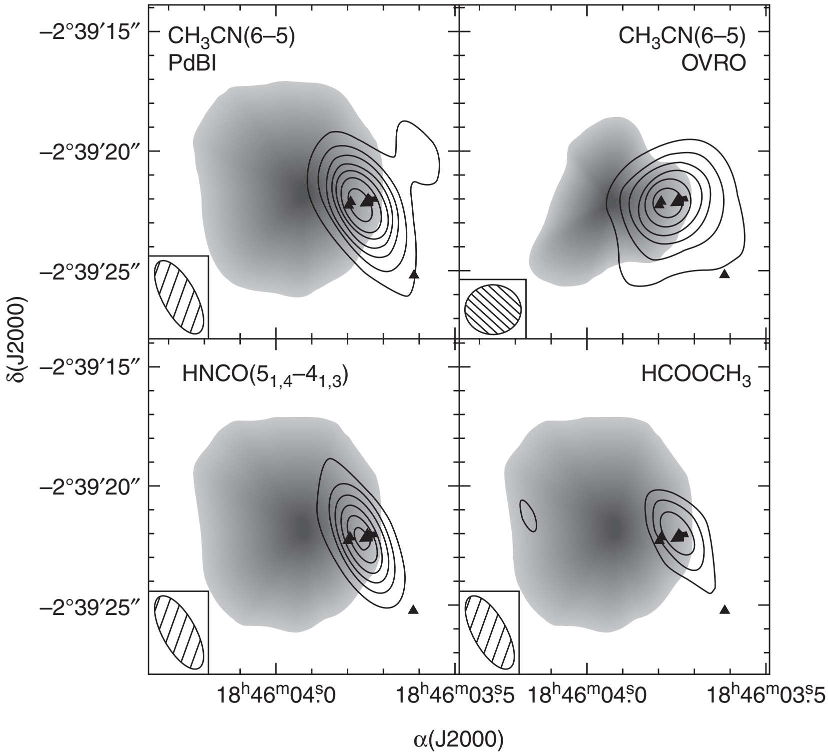

Figure 1.3. Spectra of complex molecules surrounding a massive star formation core, G29.96-0.02 (see also Chapter 5). The solid contours represent the molecular emissions and the grayscale indicates continuum emission from the ionised gas at 2.7 mm. (Reproduced, with permission, from Olmi, L., Cesaroni, R., Hofner, P., Kurtz, S., Churchwell, E., and Walmsley, C. M. 2003. *Astronomy & Astrophysics*, 407, 225.) Copyright ESO.

The first detections of extragalactic molecules were made in the 1970s. The current record for a molecular detection in a high-redshift galaxy is of CO at redshift $z = 6.42$ in 2003, in a gravitationally lensed quasar.

These detections attracted a great deal of attention, and the subjects of astrochemistry, bridging astronomy, chemistry, and physics emerged to try to account for the extraordinary range and variety of the detected species. However, there was no mere ‘stamp-collecting phase’ of molecular detections; in parallel with the development of astrochemistry, molecular emissions were immediately used to trace the existence of and physical conditions in interstellar and circumstellar gas. Such studies led to the discovery of previously unsuspected but important astronomical features – such as the GMCs in the inner part of the Milky Way. The structure of molecular outflows near cool stars

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Table 1.1. List of detected molecular species with main regions in space where they have been observed

Molecule	Source	Molecule	Source	Molecule	Source
			2 Atoms		
H_2	dm, of	AlF	circ	AlCl	circ
CO	dm, circ, cc, yso, of, eg	C_2	dm	CH	dm, eg
SH	dm	CH^+	dm, eg	CN	dm, circ, eg
HCl^+	dm	CO^+	circ, yso	CP	circ
SiC	circ, yso	HCl	cc, yso, circ	KCl	circ
NH	dm, eg	NO	cc, eg	NS	dm, yso, eg
NaCl	circ	OH	dm, circ, eg	PN	yso
SO	cc, yso, dm, circ, of, eg	SO^+	dm, eg	SiN	circ
SiO	of, circ, yso, eg	SiS	of, circ, yso	CS	cc, yso, dm, circ, of, eg
HF	dm, eg	O_2	dm, yso	CF^+	dm
PO	circ	AlO	circ	OH^+	dm, eg
CN^-	circ	SH^+	dm		
			3 Atoms		
C_3	circ, dm	C_2H	yso, cc, dm, circ, eg	C_2O	cc
C_2S	cc, eg	CH_2	yso, dm	HCN	dm, cc, yso, circ, of, eg
HCO	cc, eg	HCO^+	cc, of, yso, eg	HCS^+	cc, yso, dm
HOC^+	eg	H_2O	cc, yso, of, circ, eg	H_2S	cc, yso, of, circ, eg
HNC	dm, cc, yso, circ, of, eg	HNO	yso	MgCN	circ
MgNC	circ	N_2H^+	cc, yso, of	N_2O	dm
NaCN	circ	OCS	cc, yso, of, eg	SO_2	cc, yso, of, eg
SiC_2	circ	CO_2	yso	NH_2	dm
H_3^+	dm	SiCN	circ	AlNC	circ
SiNC	circ	HCP	circ	CCP	circ
AlOH	circ	H_2O^+	dm, yso, eg	H_2Cl^+	dm, yso
KCN	circ	FeCN	circ		

4 Atoms

H_2O_2	dm	C_3H	cc, circ, eg	C_3N	dm
C_3O	dm	C_3S	ccc, circ	C_2H_2	cc, circ
NH_3	dm, cc, yso, of, eg	HCCN	circ	$HCNH^+$	cc
HNCO	yso, eg	HNCS	cc	$HOCO^+$	dm, yso
H_2CO	dm, cc, yso, of, eg	H_2CN	cc	H_2CS	cc, yso, of, circ, eg
H_3O^+	yso, eg	SiC_3	circ	CH_3	dm
C_3N^-	circ	HCNO	yso, eg	HOCN	dm, yso
HSCN	yso				

5 Atoms

C_5	circ	C_4H	dm, cc, circ	C_4Si	circ
C_3H_2	cc, yso, circ, eg	H_2CCN	cc, yso, circ	CH_4	circ
HC_3N	cc, circ, eg	HC(O)CN	yso	HCOOH	cc, yso
H_2CNH	dm, yso	H_2C_2O	dm, cc, yso	H_2NCN	yso
C_4H^-	circ	SiH_4	circ	H_2COH^+	dm, cc

6 Atoms

C_2H_4	circ	CH_3CN	cc, yso, of, eg	HC_4H	circ, eg
CH_3NC	yso	H_2C_4	circ, cc, yso	CH_2CNH	yso
C_5H	circ, cc	HC_3NH^+	cc	CH_3C_2H	cc, yso
C_5N	circ, cc	HC_4N	circ	CH_3OH	cc, yso, eg
HC_2CHO	yso	C_3H_2O		CH_3SH	yso
NH_2CHO	yso				

7 Atoms

C_6H	circ, cc, yso	C_6H	circ, cc, yso	CH_3NH_2	yso
C_2H_3CN	cc, yso, eg	HC_5N	circ, cc	CH_3CHO	cc, yso, eg
C_2H_3OH	yso	CH_2OCH_2	yso		

(*cont.*)

Table 1.1 (*cont.*)

Molecule	Source	Molecule	Source	Molecule	Source
			8 Atoms		
H_2C_6	circ, cc, yso	HC_6H	circ, eg	C_7H	circ, cc
CH_3C_3N	cc	CH_2CCHCN	cc	NH_2CH_2CN	yso
$HCOOCH_3$	yso, of	CH_3COOH	yso,	$HOCH_2CHO$	yso
C_2H_3CHO	yso				
			9 Atoms		
CH_3C_4H	cc	CH_3CHCH_2	cc	C_8H	circ, cc
HC_7N	circ, cc	C_8H	circ, cc	C_2H_5CN	yso
CH_3CONH_2	yso	C_2H_5OH	yso, of	CH_3OCH_3	yso
			10 Atoms		
CH_3C_5N	cc	CH_3COCH_3	yso	$HOCH_2CH_2OH$	yso
C_2H_5CHO	yso				
			11 Atoms		
CH_3C_6H	cc	HC_9N	circ, cc	$HCOOC_2H_5$	yso
			12 Atoms		
C_6H_6	circ, eg	C_3H_7CN	yso		
			13 Atoms		
$HC_{11}N$	circ, cc				

Abbreviations: dm = diffuse medium (including translucent clouds); circ = circumstellar envelope around evolved star/protoplanetary nebula; cc = cold cloud core; yso = gas around a young stellar object, including observations of the hot core in the galactic centre; of = outflow; eg = extragalactic regions. Some of the abbreviations used in this list are taken from E. Herbst and E. F. van Dishoeck. 2009. *Annual Review of Astronomy and Astrophysics*, 47: 427. We do not include isotopologues in this table.

Table 1.2. Types of interstellar and circumstellar region and their physical characteristics

Region	n_{H} (cm^{-3})	T(K)
Coronal gas	$<10^{-2}$	5×10^5
HII regions	>100	1×10^4
Diffuse gas	100–300	70
Molecular clouds	10^4	10
Prestellar cores	10^5–10^6	10–30
Star-forming regions	10^7–10^8	100–300
Protoplanetary disks	10^4(outer)–10^{10}(inner)	10(outer)–500(inner)
Envelopes of evolved stars	10^{10}	2000–3500

All of the regions, except coronal gas and HII regions, can be probed with molecules.

was revealed, and molecular ices were found to be present in the interstellar medium.

Molecular emissions, along with X-ray, UV, optical, and infrared emissions, have helped to define the variety of physical states of interstellar gas. These range over at least a factor of $\sim 10^{12}$ in density and $\sim 10^5$ in temperature, from number densities of $\sim 10^{-2}$ cm^{-3} and temperatures $\sim 10^6$ K in so-called coronal gas to values of $\sim 10^{10}$ cm^{-3} and ~ 10 K in protoplanetary disks. Table 1.2 lists the known interstellar and circumstellar components. Of these types of region, diffuse clouds, molecular clouds, prestellar cores, star-forming regions, protoplanetary disks, circumstellar envelopes, and the ejecta of novae and supernovae can be studied through molecular emissions.

As astronomy moves into a new phase dominated by data from revolutionary space- and ground-based instrumentation, molecular astronomy is no longer a semidetached specialty of work in the millimetre and submillimetre regions of the spectrum. Molecular astronomy now addresses questions at the forefront of the subject, and is simply part of the range of expertise that astronomers must command. This book is intended to help astronomers become equally skilled in molecular line observations as in making observations in other regions of the spectrum.

1.3 Gas and Dust

1.3.1 Gas Composition for Interstellar Chemistry

The raw material for our considerations of chemistry consists of gas and dust. The gas consists mainly of hydrogen and helium with a small component

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Table 1.3. Approximate solar elemental abundances relative to the total number of hydrogen nuclei

Element	Abundance
H	1
He	9×10^{-2}
O	5×10^{-4}
C	3×10^{-4}
N	7×10^{-5}
Si	3×10^{-5}
Mg	4×10^{-5}
Fe	3×10^{-5}
S	1×10^{-5}
Na, Ca	2×10^{-6}

Note that solar elemental abundances may not be valid for all regions of space.

of other elements formed in stellar nucleosynthesis and distributed by novae and supernovae and by stellar winds. Obviously, the ability of a gas to form molecules involving carbon, oxygen, nitrogen, sulfur, and other elements (as well as hydrogen) depends on the abundance of the small component of other elements relative to hydrogen. These relative elemental abundances may vary from place to place within a galaxy and from galaxy to galaxy. Solar abundances are often used as a conventional reference level; solar elemental abundances relative to hydrogen are shown in Table 1.3. Gas with these relative elemental abundances is said to have solar *metallicity*. The metallicity is an important parameter in astrochemistry; we consider the effect on the chemistry of varying the metallicity in Chapter 4. It is often assumed that although the metallicity may vary, the abundances of the elements relative to each other follow solar values. However, this may not be the case everywhere. For example, if considering the early Universe, supernovae of different masses may lead to quite different predictions of relative abundances of the major elements carbon, nitrogen, and oxygen. Stellar evolution models for initially zero-metallicity gas predict nitrogen to be underabundant whereas oxygen and magnesium are overabundant compared to solar metallicity. Also, dredge-up processes in evolved stars are observed to create distinct differences in elemental abundances. For example, some stars may have different C:O ratios in their atmospheres and envelopes at different evolutionary stages. There are examples of a stellar atmosphere being at one stage carbon-rich and at another oxygen-rich. Thus, the relative elemental abundances to be used are not always solar.

1.3.2 Dust

Dust is observed to be mixed with interstellar gas in all galaxies. It is detected either through the extinction that it causes at UV, optical, and infrared wavelengths (see Figure 1.4), or by the detection of thermal emission from warm dust in the vicinity of stars and from cooler dust in dark clouds. Dust is also present in the envelopes of cool stars and of novae and supernovae; these are the locations where dust is believed to nucleate and grow. The observations on long low-density paths in the Milky Way Galaxy require that dust grains range in size, a, from about a nanometre to about a micron, with number density $n_d(a)da$ in the range a to $a + da$ heavily weighted to the smaller grains; $n_d(a)da \sim a^{-3.5}da$. The grains are asymmetric in shape, and the larger grains (at least) can be partially aligned by the local magnetic field. The smallest grains may be molecular (rather than bulk) in nature and may include polycyclic aromatic hydrocarbons (PAHs) with some graphitic-type structure. The chemical composition of grains includes carbons of both ring and polymeric structures, amorphous and crystalline silicates, and probably various other metallic oxides.

From the perspective of this book, we shall be concerned with the various roles of dust in the interstellar medium. Its primary role is to extinguish UV and visual radiation in the interior of gas clouds, thereby shielding interior material from the destructive effects of starlight. Some of the absorbed radiation releases photoelectrons from the dust grains; these are an important energy source for the gas. Optical and UV starlight that is absorbed heats the grains, which then radiate in the far-IR (see Figure 1.5). Another important role of dust is in catalysing reactions on grain surfaces, especially the formation of molecular hydrogen, and contributing product molecules to the network of gas reactions. In some darker regions, icy mantles accumulate on the surfaces of dust grains; these mantles are sinks for molecules, removing them from the gas. The mantles are observed to contain water, carbon dioxide, carbon monoxide, methanol, and other species. Chemical processing can also be formed in these ices, making molecular species of greater complexity than can easily occur in the gas phase. Thermal and nonthermal processes may return the ices to the gas phase. Dust grains also tend to 'mop up' electrons from the gas, thereby affecting the gaseous ionisation level (and consequently the gas-phase chemistry) within interstellar clouds.

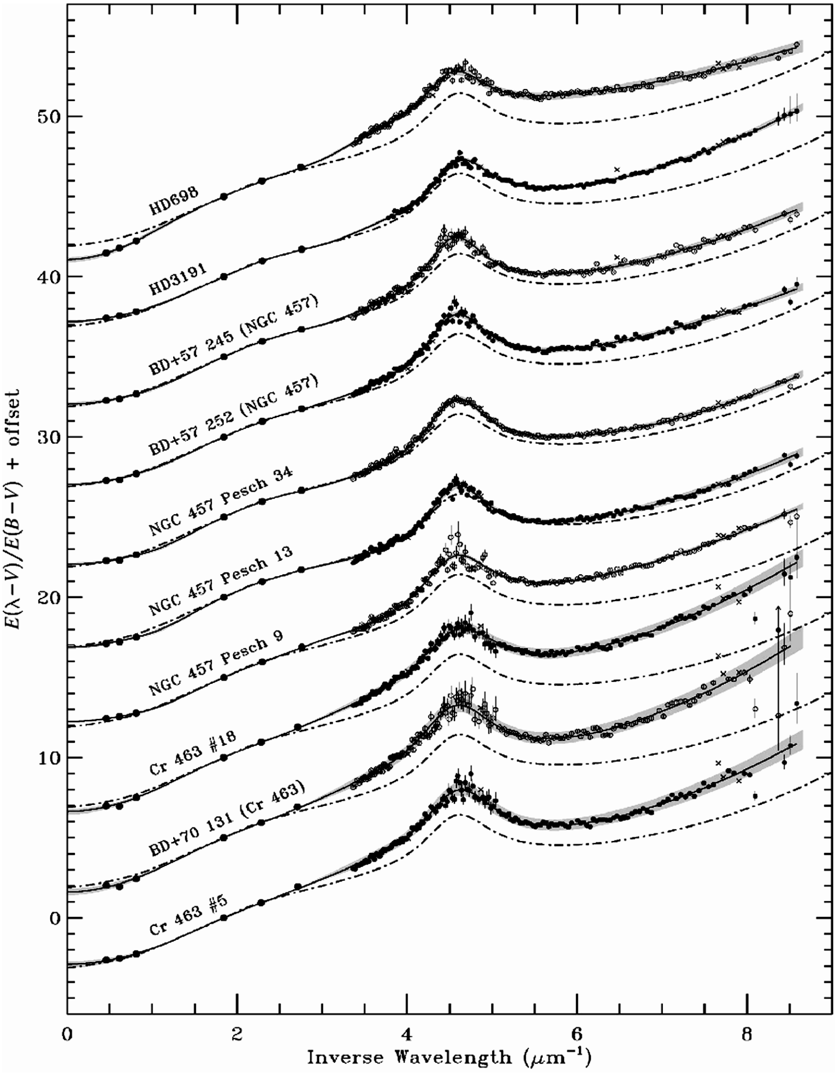

Figure 1.4. Interstellar extinction curves (offset for clarity) for lines of sight towards a number of bright stars in the Milky Way. The curves are normalised, but they all have the same basic shape – higher extinction in the UV than in the IR and a near linear part in the visual. This requires a distribution of grain sizes, with many more small grains than large. The dot-dash curve is the mean interstellar extinction curve. (Reproduced by permission of the AAS from Fitzpatrick, E. L., and Massa, D. 2007. *Astrophysical Journal*, 663, 320.)

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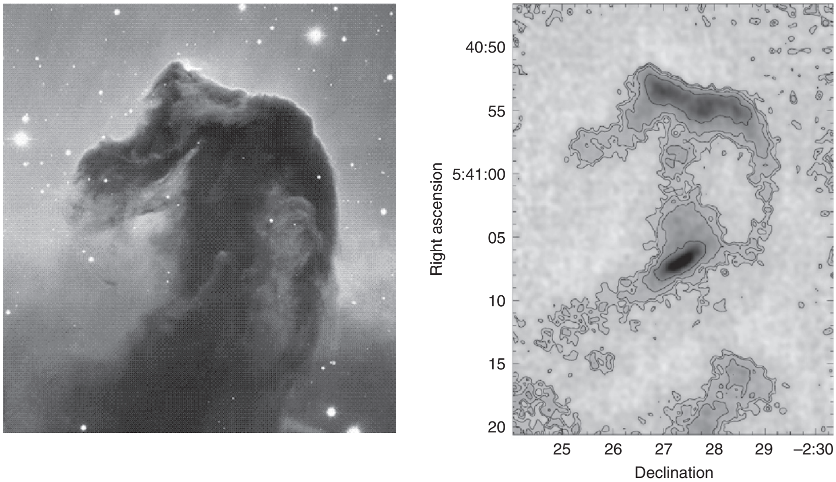

Figure 1.5. The Horsehead Nebula (left) optical image from the VLT (ESO) and (right) the JCMT-SCUBA 850 μm contour map. The bright submillimetre regions indicate emission from prestellar objects. (Reproduced with permission from Ward-Thompson, D., Notter, D., Bontemps, S., Whitworth, A., and Attwood, R. 2006. *Monthly Notices of the Royal Astronomical Society*, 369, 1201.)

Although the chemical nature and physical structure of the dust are undoubtedly important for all these topics, we do not discuss them here. We do not describe other dust properties, nor the origin of dust in supernovae, novae, and other stellar winds, but simply refer to relevant works on the subject (see Further Reading).

However, it is important to note that the grains lock up a significant fraction of certain elements; for example, models of interstellar extinction in the Milky Way Galaxy require that almost all of the element silicon is in silicate dust, whereas a significant fraction of carbon, up to perhaps one half, is in carbon dust. Clearly, those atoms locked in the dust are not available for gas-phase chemistry unless the grains are being eroded in high-temperature gas. If not, then the solar abundances shown in Table 1.3 are not wholly available for chemistry in the gas phase and need to be adjusted to allow for the components locked in the dust.

Finally, like metallicity, the dust:gas ratio is not a fixed parameter. The quantity of dust is a consequence of the history of stellar evolution, so may vary within and between galaxies. Although the ratio is difficult to determine accurately, it is probably related to the metallicity and may vary from one galaxy to another, or even within one galaxy. The dust:gas ratio in nearby external galaxies appears to correlate fairly well with metallicity. The range in

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each parameter for these objects appears to be around one order of magnitude. We discuss the importance of these parameters in Chapter 4.

1.4 What's in This Book

To address the questions posed in the previous sections, astronomers need some understanding of how interstellar chemistry works. Chapter 2 gives a brief summary of the basic language that we use to discuss molecular spectroscopy as a tool in molecular astrophysics. Many readers will have met this material elsewhere and may wish to omit the chapter. Then Chapter 3 summarizes interstellar chemistry and describes rather concisely the network of reactions that generates the molecular species observed (and many that are not yet detected).

The starting point is assumed to be a dusty atomic gas in which, by a variety of processes, molecules are to be formed. However, an undisturbed cold gas of cosmic composition is chemically almost inactive, and to generate useful tracer molecules on a reasonable timescale an efficient chemistry needs to be switched into action. The necessary switch, or *driver*, may be starlight, cosmic rays, surface reactions on dust grains, or gas dynamical processes. Both starlight and cosmic rays can act as sources of energy capable of generating ionisation and heat in the gas so that a chemistry may be initiated. Grain surfaces can catalyse new products from atoms and molecules arriving at the surface. Gas dynamical processes such as shocks or turbulent interfaces may introduce heat and possibly ionisation into the gas, initiating a characteristic chemistry.

In Chapter 4 the sensitivity of the chemistry to particular influences is explored. Do characteristic 'signature' molecules arise when a particular driver of the chemistry is enhanced above a conventional level? We look in particular at regions in which the stellar radiation is especially powerful, at dense cold regions, and at turbulent interfaces between cold and hot moving gases. We also ask: What happens to the chemistry if the dust:gas ratio or the elemental abundances depart significantly from canonical values?

Chapter 5 applies the ideas developed in the previous chapters to several important and much-studied situations in the Milky Way: these are molecular clouds and star-forming regions where either low-mass or high-mass stars are being formed. For each of these regions, the main question posed is this: What are the most appropriate tracer molecules to use in probing these situations?

In Chapter 6 we apply the ideas developed so far to interstellar gas in external galaxies. In these situations, a much wider range of physical conditions may occur compared to those in the Milky Way because the drivers of the chemistry, such as cosmic ray flux or starlight intensity, the dust:gas ratio, or the elemental abundances, may themselves be very different from Milky Way values. What are the molecules that allow observers to probe those drivers? Can we infer values of those physical quantities in distant galaxies?

In Chapter 7 we peer into the early Universe and review the role of molecules in pregalactic astronomy, and we speculate on the possibility of detecting molecules during the very early events of the history of the Universe.

It is, however, a significant step from raw data taken at the telescope to information on, say, molecular column densities that is astronomically useful. Chapter 8 describes the conventional approaches that allow the observer to convert data from the telescope to useful measures such as molecular column densities or fractional abundances and to obtain measures of density and temperature. Chapter 9 summarises current numerical approaches to radiative transfer. From measures such as these the astronomer may infer masses and begin to make useful speculations. Finally, Chapter 10 provides information for some molecular transitions often used as tracers of different types of interstellar and circumstellar regions.

1.5 Further Reading

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