Carnegie Observatories Astrophysics Series, Vol. 4:
Origin and Evolution of the Elements, 2004
ed. A. McWilliam and M. Rauch (Cambridge: Cambridge Univ. Press)

Molecules in the Interstellar Medium

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Abstract

The molecular component of the interstellar medium contains more than 120 molecular species and represent the coldest, densest, and most obscured part of the interstellar gas. Molecules are the only probes of the physical and chemical conditions in these obscured regions and allow us to study the earliest stages of star formation. Molecules and the molecular chemistry also strongly influence the physical conditions, mainly by acting as efficient cooling agents. In this overview, the main characteristics of the molecular component of the interstellar medium is reviewed. Some outstanding problems are discussed, together with a summary of challenges for the future.

1.1 Introduction

The molecular component of the interstellar medium (ISM) represents the coldest and densest part of the ISM. Molecular gas is distributed in discrete clouds, which can be self-gravitating and directly involved in the formation of new generations of stars. These cold and dense regions can only be probed at far-infrared and longer wavelengths. Photons from molecular transitions can reach us from the densest and most opaque parts and can be used to trace the physical structure of the clouds, as well as allowing a detailed study of the dynamics of the stellar formation processes. Molecular transitions can also be used to derive the magnetic field strength and the cosmic ray ionization rate.

Interstellar molecules are the result of dynamic chemical processing in the ISM itself. The conditions found in the ISM are difficult or impossible to achieve in terrestrial laboratories, and the molecular ISM is therefore a unique laboratory where exotic reactions can be studied. Indeed, several molecular species were first detected in interstellar space before they were synthesized in laboratories on Earth. The interstellar molecules are diagnostics of the chemical evolution, and their abundances reflect the raw material that will ultimately be part of the formation of protoplanetary disks and planetary systems. The molecules are, however, not just passive probes. They are important cooling agents for the gas and directly influence the hydrodynamical gas evolution.

1.1.1 Historical Background

The existence of molecules in interstellar space has been known for almost 70 years. The first detection of the molecules in the ISM was done through observations of both narrow and broad absorption lines seen toward bright stars (Merrill 1934, 1936). It was quickly realized that these lines did not originate from some unknown atomic species in the atmosphere of the stars. The first suggestion that these lines were of molecular origin was made by Russell (1935). Swings & Rosenfeld (1937) found a theoretical match with electronic transitions of a few diatomic molecules. This suggestion was put on firm grounds through the observational work of McKellar (1940), who positively identified several lines as due to the molecules CH^+, CH, and CN. Meanwhile, more diffuse lines had been detected by Beals & Blanchet (1938). In a provocative paper by Swings & Öhman (1939), these lines were tentatively identified with small crystals or amorphous aggregates of light elements, such as solid hydrogen, oxygen, or ice of CO_2.

By the early 1940s a few simple diatomic molecules were known to exist in interstellar space, their number densities had been estimated with a surprising accuracy, and their excitation temperatures were known (e.g., McKellar 1940; Adams 1941). In fact, through observations of electronic transitions of adjacent rotational levels of CN, it was established that the "effective temperature of interstellar space" was around 3 K. These early observers of the molecular component of the ISM had, unwittingly, made the first measurement of the temperature of the cosmic microwave background radiation, not to be discovered for another 25 years.

After this initial flurry of observational and theoretical work, not much was done concerning the molecular component of the ISM until interstellar OH was discovered in 1963 (Weinreb et al. 1963). This time the observations were done using the new technique of radio astronomy. Just as the early optical observations, the radio OH line was initially seen in absorption, but was soon found to also exhibit strong maser emission. It was still believed that only simple diatomic molecules could exist in the harsh environment of interstellar space. During the following 10 years, however, there were radio detections of more complex molecules, such as ammonia NH_3 (Cheung et al. 1969) and formaldehyde H_2CO (Snyder et al. 1969). In 1973 the abundant CO molecule was discovered (Wilson, Jefferts, & Penzias 1970), as well as several radio lines of CH (Rydbeck, Elldér, & Irwine 1973).

With the introduction of telescope and receiver systems capable of observing in the 100–200 GHz frequency range (corresponding to wavelengths of 3−1 mm), many new molecules, with increasingly complex structure, were detected in a rapid pace. The reason for this rapid development is the richness of molecular rotational transitions with energies corresponding to this wavelength range, coupled with the cold excitation conditions of interstellar space as depicted by McKellar and Adams 40 years earlier.

1.1.2 Present Status

Today there are more than 120 molecular species known to exist in interstellar space (see Table 1.1), and the list continues to grow as instruments become more sensitive and as studies in terrestrial laboratories allow more lines to be identified in already obtained spectra. Several of the more prominent molecule-rich hot cores have been part of so-called spectral scans (e.g., Nummelin et al. 1998). The complexity of the detected molecules has grown from simple diatomic molecules to those containing up to 13 atoms. Although the heaviest molecules observed to date consist of long carbon chains, some molecules have a more intricate structure. One example of the latter is the recently detected glycolaldehyde CH_2OHCHO, an interstellar monosaccharide sugar compound (Hollis, Lovas, & Jewell 2000). Some molecular species remain only tentatively detected, although they are believed to exist in the molecular ISM. An example of these species is glycine, the simplest amino acid (NH_2CH_2COOH). Several searches for it have been done. The main difficulty in detecting glycine is the large number of allowed transitions and the line confusion that limits the observed spectral sensitivity. Some light hydrides also remain undetected, mainly because their ground transition fall at wavelengths inaccessible to existing telescopes and instruments. The LiH molecule has, however, been tentatively detected at a redshift $z = 0.68$ (Combes & Wiklind 1998), by virtue of being redshifted into an observable wavelength regime.

The field of molecular astrophysics has grown to involve and impact almost all branches of astrophysics. Astrochemistry tells about how molecules are formed and which processes are important in different environments. Molecular emission and absorption lines can be used to determine the detailed physical conditions of the interstellar gas in which the molecules reside. In this case it is necessary to follow the transfer of radiation in great detail. The cooling provided by the molecular gas is of paramount importance in the formation of stars.

The molecules in the ISM are thus not just a probe of the conditions, but take an active part in regulating the temperature of the gas. In order to understand complex processes such as star formation, it is therefore necessary to study the interplay between molecules, its chemistry, the transfer of radiation, and the effect the molecules have on the dynamical process itself. The simultaneous solution of molecular astrochemistry, transfer of radiation, and hydrodynamics has not yet been achieved, but when it is done it is likely to give us a good understanding of how stars are formed.

1.2 Components of the Molecular ISM

1.2.1 Molecular Species

Astrochemists usually divide the molecular species found in the ISM into organic and inorganic molecules. The organic ones are simply those containing carbon, while the inorganic do not. The vast majority of detected molecules in the ISM are organic (see Table 1.1). The organic molecules can be divided into simple diatomic molecules, such as CO, CH, CS, etc., and more complex hydrocarbons, such as methanol (CH_3OH), ethyl alcohol (CH_3CH_2OH), etc.

Most of the interstellar molecules are linear in shape: examples of linear molecules are CO, CH_3OH, CH_3CH_2OH, and HC_9N. A few species of ring molecules have now also been detected: C_3H, C_3H_2, C_2H_4O, and SiC_2. There are also some molecules that have only been seen in circumstellar envelopes and are therefore not part of the ISM proper: examples of these are MgCN, AlF, and KCl. On the other hand, many of the molecules found in the ISM are also found in circumstellar envelopes.

In general, molecules with a simple structure have fewer symmetries and therefore a smaller number of transitions than more complex molecules. Molecules with several symmetries, and a correspondingly large number of transitions can be difficult to identify since the line strength in any particular line will be low. Also, these complex molecules with many low-intensity lines contribute significantly to confusion. This is especially true in molecular clouds with rich chemistries.

There are three main types of transitions between different energy levels of a molecule: (1) electronic transitions with $\Delta E \approx$ a few eV, corresponding to UV/optical wavelengths, (2) vibrational transitions with $\Delta E \approx 0.1 - 0.01$ eV, corresponding to near-infrared/infrared

Table 1.1. *Known Interstellar and Circumstellar Molecules*

Hydrogen compounds					
H_2	H_3^+				
Hydrogen and carbon compounds					
CH	CH^+	C_2	CH_2	C_2H	C_3
CH_3	C_2H_2	C_3H	c-C_3H	CH_4	c-C_3H_2
H_2CCC	C_4H	C_5	C_2H_4	C_5H	H_2C_4
CH_3C_2H	C_6H	H_2C_6	C_7H	CH_3C_4H	C_8H
Hydrogen, carbon, and oxygen compounds					
OH	CO	CO^+	H_2O	HCO	HCO^+
HOC^+	C_2O	CO_2	H_3O^+	$HOCO^+$	H_2CO
C_3O	CH_2CH	HCOOH	H_2COH^+	CH_3OH	HC_2CHO
C_5O	CH_3CH_2OH	c-C_2H_4O	CH_3OCHO	CH_2OHCHO	CH_3COOH
CH_3OCH_3	CH_3CH_3OH	$(CH_3)_2CO$			
Hydrogen, carbon, and nitrogen compounds					
NH	CN	NH_2	HCN	HNC	N_2H^+
NH_3	$HCNH^+$	H_2CN	HCCN	C_3N	CH_2CN
CH_2NH	HC_2CN	HC_2NC	NH_2CN	C_3NH	CH_3CN
CH_3NC	HC_3NH^+	C_5N	CH_3NH_2	CH_2CHCN	HC_5N
CH_3C_3N	CH_3CH_2CN	HC_7N	CH_3C_5N	HC_9N	$HC_{11}N$
Sulphur containing compounds					
SH	CS	SO	SO^+	NS	SiS
H_2S	C_2S	SO_2	OCS	HCS^+	H_2CS
HNCS	C_3S	CH_3SH	C_5S		
Other compounds					
SiH	SiC	SiN	SiO	HCl	NaCl
AlCl	KCl	HF	AlF	CP	PN
c-SiC_2	NaCN	MgCN	MgNC	$HSiC_2$	SiC_3
SiH_4	SiC_4	NO	HNO	N_2O	HNCO
NH_2CHO					

Molecules preceded by "*c*–" are ring-shaped.

wavelengths, and (3) rotational transitions with $\Delta E \approx 10^{-3}$ eV, corresponding to mm/submm wavelengths. There are also other, less frequent modes, such as bending transitions.

The bulk of the molecular gas is characterized by very low kinetic temperatures, 5–100 K. Since the molecular gas is shielded from UV radiation by dust grains and, for the most abundant molecules, through self-shielding, the main excitation mechanism is collisions with H_2. With the low kinetic temperatures, usually only the rotational levels will be populated. Vibrational and electronic transitions can occur in warm molecular gas, at the periphery of molecular clouds, and in photo-dissociation regions (see § 1.2.2).

1.2.2 Molecular Clouds

Already the first observers of interstellar molecules realized that they occurred in discrete clouds rather than being spread over large volumes as in the case for warm ionized gas (e.g., Adams 1948). Clouds containing molecules are divided into different types, on a somewhat *ad hoc* basis. There are five main types of molecular clouds: diffuse, translucent, dark, giant molecular cloud (GMC), and hot cores. Their properties are listed in Table 1.2. In addition, molecules can be found in photo-dissociation regions or photon-dominated regions (PDRs). PDRs exhibit a relatively rich chemistry, driven by the photon field. In principle,

Table 1.2. *Types of Molecular Clouds*

Type of Cloud	A_V (mag)	n (cm^{-3})	T_k (K)	Contents
Diffuse	<1	10–100	50–100	simple molecules, atoms, ions
Translucent	1–5	$100–10^3$	20–50	ions, more complex molecules
Dark	>5	$> 10^3$	10	hydrocarbons, few ions
GMC	large	$\sim 10^3$	20–40	mix of different types of clouds
Hot core	large	$> 10^4$	40–100	rich chemistry

any of the clouds listed in Table 1.2 becomes a PDR if it is exposed to a high flux of UV photons. The chemistry and physical conditions will, however, change as the photo-processes start to dominate the chemistry. The sizes of molecular clouds can vary from less than 1 parsec for the smallest cores to 100 pc for the largest GMCs. There are indications that very small-scale structure ($\sim$10 AU) exists in the molecular ISM (e.g., Rollinde et al. 2003).

In reality, it is rare to encounter a single isolated molecular cloud that can be classified according to the above types. In most cases, the molecular gas exist in a complicated mixture of different physical conditions. A part of a cloud complex can be a typical dark cloud, while the surroundings are more characteristic of translucent gas. Also, the topology of molecular clouds is in most cases complicated, often showing a filamentary structure. Work by Falgarone and collaborators has shown that over several orders of magnitude, molecular gas can have a self-similar structure (Puget & Falgarone 1990; Falgarone et al. 1998). The inhomogeneous structure of the molecular gas can have profound effects on the chemistry and the excitation conditions of the molecules, as UV photons can penetrate deeper into the cloud complex. This will be discussed further in § 1.4.

1.3 Molecular ISM Chemistry

When the first molecules were discovered in 1934, it was not known whether they were formed *in situ* or originated from stellar atmospheres. It was known that molecules, such as TiO, exist in cool stars, and with a sufficiently strong stellar wind, the ISM could in principle be enriched by molecules. Today we know that the vast majority of all molecules originate in the ISM. The number of molecules coming from circumstellar envelopes is very small indeed. The contribution of dust grains from circumstellar envelopes and Type II supernovae, however, is significant and also necessary in order to start the production of ISM molecules.

There are two types of chemical processes driving the chemistry in the ISM: gas-phase reactions and grain-phase reactions. The grain-phase reactions are important, but not yet fully understood. They involve surface migration of the atoms and molecules, sticking coefficients and desorption efficiencies. Gas-phase reactions, on the other hand, are quite well known and can successfully be modeled. However, as will be seen in § 1.4, a successful modeling of the chemistry of molecular gas needs both gas- and grain-phase reactions to be able to accurately predict molecular abundances.

In principle, there are only nine processes with which molecular bonds can be formed, rearranged, or destroyed (see Table 1.3). Which ones dominate in any given situation depends on the type of clouds where the chemistry is taking place (e.g., the flux of UV photons,

Table 1.3. *Molecular Bond Processes*

radiative association	A + B	$\rightarrow$	AB + $h\nu$	
associative attachment	A^- + B	$\rightarrow$	AB + e	bond formation
grain surface formation	A + B:g	$\rightarrow$	AB + g	
neutral–neutral	A + BC	$\rightarrow$	AB + C	
ion–molecule	A^+ + BC	$\rightarrow$	AB^+ + C	bond rearrangement
charge transfer	A^+ + BC	$\rightarrow$	A + BC^+	
photodissociation	AB + $h\nu$	$\rightarrow$	A + B	
dissociative recombination	AB^+ + e	$\rightarrow$	A + B	bond destruction
collisional dissociation	AB + M	$\rightarrow$	A + B + M	

density of ions and electrons, etc.). On the other hand, there are up to 400 different molecular species that needs to be considered when modeling the chemistry, and the total number of reactions can be around 4000 (e.g., Millar, Farquhar, & Willacy 1997; van Dishoeck 1998). Each reaction proceeds at a rate that can be a function of temperature. A reaction is governed by a rate equation, which defines the abundance n of a given molecule (e.g., Duley & Williams 1984). The result is a chemical reaction network consisting of 4000 coupled nonlinear differential equations. Equilibrium chemical models are used to study the steady-state chemical properties of molecular gas and the influence of varying degrees of UV extinction. Full time-dependent models have become more common, and can allow for self-consistent solutions involving changing physical parameters such as density and temperature (e.g., Bergin & Langer 1997). The time-dependent models are important since the chemical time scales often are of the same order as the dynamical time scales for molecular gas. A goal with astrochemistry is to use certain key molecules as diagnostic of the temporal evolutionary state of a molecular gas entity: a star-forming molecular cloud, a protostellar core, or a protoplanetary disk (e.g., van Dishoeck & Blake 1998; Doty et al. 2002).

There are now also models that incorporate gas-grain chemistry where molecules are accreted, formed, and desorbed from grain surfaces (e.g., d'Hendecourt, Allamandola, & Greenberg 1985; Hasegawa & Herbst 1993a, b; Roberts & Herbst 2002). Since it is not easy to reproduce the interstellar conditions in terrestrial laboratories, progress in understanding the grain surface chemistry and its connection to the gas phase has been slow. As will be seen in § 1.4, the grain chemistry is most likely very important for a complete understanding of astrochemistry, as well as for understanding the stellar formation process.

1.3.1 Molecular Absorption

The very first molecular observations were done using absorption lines, both at optical and radio wavelengths. The use of absorption lines is, however, difficult at radio and millimeter wavelengths due to the fact that the necessary background continuum sources generally have an angular extent much smaller than the telescope beam. It was only with the introduction of millimeter interferometry techniques that molecular absorption-line studies could be done in earnest.

The main difference between absorption- and emission-line observations at millimeter wavelengths is that while molecular emission lines need a relatively dense and warm gas in order to produce an observable signal (the observed signal is approximately proportional to the temperature characterizing the level population), absorption-line measurements are most sensitive to the cold and diffuse molecular component, where the observed signal $\propto (\mu_0/T)^2$, where μ_0 is the permanent electric dipole moment of the molecule (e.g., Wiklind & Combes 1997b). The dependence of the opacity on the permanent dipole moment implies that less abundant molecules can be as easily detectable as more abundant ones, if their permanent dipole moment is larger. For instance, the HCO^+/CO abundance ratio is approximately 5×10^{-4}, yet HCO^+ can be more easily detected in absorption than CO.

Using the IRAM Plateau de Bure millimeter-wave interferometer, the molecular abundances in diffuse molecular gas in the Milky Way galaxy has been extensively explored using the technique of absorption lines (e.g., Lucas & Liszt 1996, 2002; Liszt & Lucas 1998, 2002). Molecular absorption lines have also been used to probe the detailed properties of molecular gas in galaxies up to redshifts of $z \approx 0.9$ (Wiklind & Combes 1994, 1999; Combes & Wiklind 1997, 1999; Menten, Carilli, & Reid 1999). The results from these studies show that molecular abundances in Galactic diffuse clouds are similar to that of dark clouds. Furthermore, for both nearby and distant systems, some molecules have much higher abundances than what is suggested by chemical models. For instance, HCO^+ is found to be up to 100 times more abundant in diffuse molecular gas than indicated in models. This clearly shows that conventional models of gas-phase chemistry in low-density and moderate-extinction regions cannot account for all the processes taking place.

1.4 The Missing Ingredients

Gas-phase chemical models, especially the ion-molecule reaction scheme, have been very successful in explaining the abundances of simple hydrocarbons in diffuse and translucent clouds, the high abundances of protonated ions such as HCO^+ and N_2H^+, seen in emission, as well as the high abundances of unsaturated and metastable molecules in dark clouds. The models also explain the high isotopic fractionation found for many species, in particular the deuterium fractionation (e.g., Millar, Bennett, & Herbst 1989; Millar 2002). However, as mentioned in § 1.3.1, absorption-line measurements indicate abundances for some molecular species that are higher than what the chemical models suggest.

There are also a few molecules that are important ingredients in the chemical modeling, as well as important for the constraining the physical properties of the gas itself, which have yet to be detected. Among these are water vapor, H_2O, and molecular oxygen, O_2. Chemical models predict high abundances of these species in dark molecular clouds, but they have remained impossible or difficult to observe due to their presence in the terrestrial atmosphere.

1.4.1 Molecular Oxygen

Oxygen is the third most abundant element in the Universe and is an important part of the interstellar molecular chemistry. The simplest oxygen-bearing molecule is molecular oxygen, O_2, which is believed to be an important cooling agent for molecular gas (e.g., Goldsmith & Langer 1978) and thus important for the formation of stars.

The formation and destruction pathways for O_2 are fairly simple and well known (e.g., Black & Smith 1984; Bergman 1995). In dark quiescent clouds, the O_2 abundance should reach $\sim 20\% - 40\%$ of that of CO. Despite its predicted high abundance, O_2 remains undetected in the ISM. The transitions of O_2 are mostly obscured by the Earth's atmosphere. Early upper limits to its abundance were therefore obtained through observations of isotope

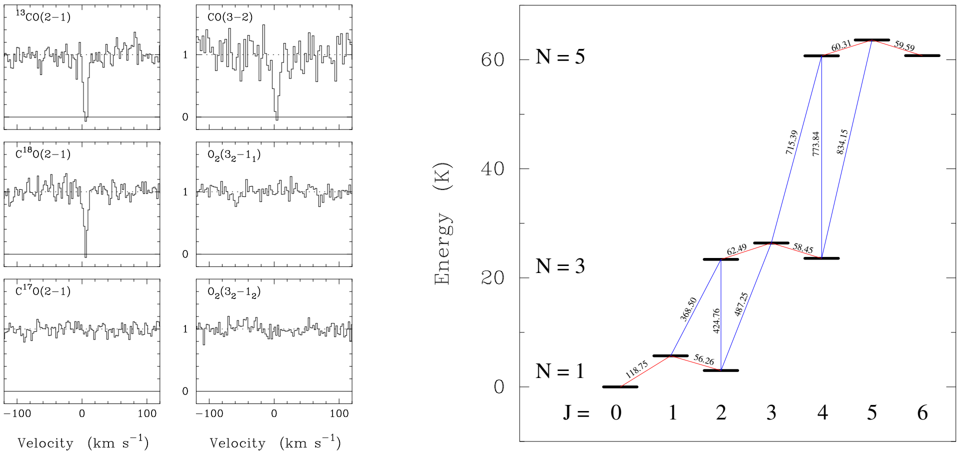

Fig. 1.1. *Left:* Molecular absorption lines of rotational transitions seen toward B0218+357 at $z = 0.685$ (Wiklind & Combes 1995). The left three panels show absorption of ^{13}CO(2-1), C^{18}O(2-1), and a nondetection of C^{17}O(2-1). The right hand panels show ^{12}CO(2-1) on the top and nondetections of the $N_J = 3_2 - 1_1$ and $N_J = 3_2 = 1_2$ transitions of O_2 (Combes & Wiklind 1995; Combes, Wiklind, & Nakai 1997). *Right:* Energy level diagram for molecular oxygen, O_2. The transition frequencies in GHz are shown, as well as the energy levels in K (E/k).

variants, ^{16}O^{18}O (Goldsmith et al. 1985; Liszt & vanden Bout 1985; Pagani, Langer, & Castets 1993; Maréchal et al. 1997a). Observations of the main isotope from redshifted objects have been obtained through emission studies (Liszt 1985, 1992; Goldsmith & Young 1989) as well as absorption-line studies (Combes & Wiklind 1995; Combes, Wiklind & Nakai 1997).

The best upper limit to the O_2 abundance was obtained through molecular absorption lines (see also § 1.3.1) in the $z = 0.68$ intervening system toward the background QSO B0218+357 (Combes & Wiklind 1995; Combes et al. 1997). Additional observations of ^{12}CO, ^{13}CO, ^{18}CO, and a nondetection of ^{17}CO led to an upper limit of N(O_2)/N(CO) $< 2 \times 10^{-3}$ (Fig. 1.1). The theoretical value of the abundance ratio O_2/CO is quite insensitive to the density and extinction and is $\sim$0.4 (Maréchal, Viala, & Banayoun 1997b). Adopting a typical Galactic CO/H_2 abundance ratio of 5×10^{-4}, the observed upper limit corresponds to an O_2 abundance a few times $< 10^{-7}$. This is almost 3 orders of magnitude lower than predicted ISM abundances and was a first indication that the chemistry in the ISM may have surprises in store.

Recently, two satellites have provided new data on the abundance of interstellar O_2: *SWAS* (the *Submillimeter Wavelength Astronomy Satellite*) launched in 1998 (Melnick et al. 2000), and *Odin* launched in 2001 (Hjalmarson et al. 2003). Both satellites carry a small submillimeter telescope above the obscuring terrestrial atmosphere. While both *Odin* and *SWAS* could observe the higher transition, $N_J = 3_3 - 1_2$ (see Fig. 1.1), *Odin* also carried a detector for the ground transition at 118.75 GHz, $N_J = 1_1 - 1_0$, allowing for a better sensitivity. Neither satellite detected the O_2 molecule, despite heroic efforts (Goldsmith et al. 2000; Pagani et al. 2003). The best 3 σ upper limits for the N(O_2)/N(H_2) ratio are $< 2.6 \times 10^{-7}$ for *SWAS*

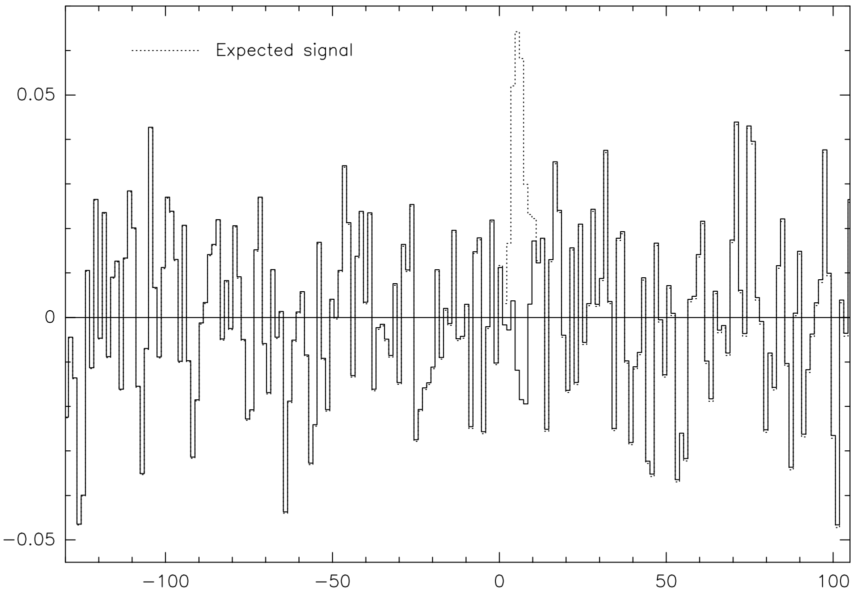

Fig. 1.2. *Odin* spectra of the ground transition of O_2 toward ρ Oph (Pagani et al. 2003). The dotted line indicates a previously reported tentative O_2 detection by *SWAS*. The detection is not confirmed by the more sensitive *Odin* data.

(Goldsmith et al. 2000) and $< 1.0 \times 10^{-7}$ for *Odin* (Pagani et al. 2003). The value expected from chemical models of dark clouds is $N(O_2)/N(H_2) = (2-5) \times 10^{-4}$. A tentative detection of O_2 emission reported by *SWAS* (Goldsmith et al. 2002) in an outflow region of the ρ Oph cloud was not confirmed with *Odin* data (Pagani et al. 2003), despite a better noise level (Fig. 1.2).

1.4.2 Reasons for O_2 Nondetections.

There are several possible explanations to the low O_2 abundances found by *SWAS*, *Odin*, and through molecular absorption lines. Not all of the explanations give results that are consistent with other abundances, notably the low water vapor abundances also found by *SWAS* and *Odin*.

High C/O ratio. The simplest way to decrease the O_2 abundance is to increase the C/O abundance ratio from its nominal cosmic abundance value of 0.45. An increase in C/O by a factor $\sim$2 decreases the O_2 abundance by a factor 150 (Maréchal et al. 1997b). This is accompanied by a similarly large decrease in the H_2O abundance as well as in the OH abundance. The reason for the O_2 abundance dependence on the C/O ratio is simply that if C/O$<$1 there are oxygen atoms left when all the gas-phase carbon has been bound up in CO, leaving enough gas-phase oxygen to build other molecules. However, even in the densest and most opaque clouds, the atomic oxygen remains more abundant than O_2 and represents between 20% and 30% of the available gas-phase oxygen (Maréchal et al. 1997b).

Clumpy cloud structure. Molecular oxygen is easily photo-dissociated and therefore not expected to be abundant in diffuse gas or in PDRs. Spaans & van Dishoeck (2001) computed models of the thermal and chemical balance of molecular gas with a clumpy cloud structure and exposed to UV radiation, where the abundances of O_2 and H_2O were computed for various density distributions, radiation field strengths, and geometries. They found that an inhomogeneous density distribution lowers the column density of both H_2O and O_2 compared to the homogeneous case by more than an order of magnitude for the same A_V. In particular O_2 is sensitive to the penetrating UV radiation, and the destruction of O_2 remains dominated by photodissociation to large extinction as the clumpy structure allows UV photons to penetrate to larger depths.

Dust coagulation. Casu, Cecchi-Pestellini, & Aiello (2001) argue that dust coagulation in dense clouds can alter the amount of UV photons that penetrate deep into the cloud interior. This model agree with some observational evidence that the UV-to-visual extinction is smaller in dense clouds than in more diffuse clouds. This could affect molecules like O_2 and H_2O, which are susceptible to photodissociation, while a more abundant molecule like CO would be protected through self-shielding. This model predicts that the main carrier of oxygen in dense molecular clouds should be atomic oxygen, while CO is the main carrier of gas-phase carbon. Another interesting, and testable, effect is an increase of the HOC^+/HCO^+ ratio by a factor $\sim$100.

Diffusive mixing and turbulence. Turbulence is the dominant component of support and dynamics of most molecular clouds. It may also play a role in the mixing of material. If this is the case, chemical abundances will be altered compared to static models if the transport time scale between zones is less than the chemical time scale. Willacy, Langer, & Allen (2002) couple diffusion and gas-grain interaction (freeze-out) as well as photodissociation processes. They find that diffusive processes significantly alter the predicted chemical abundances. Increases in the abundances of C I and C II and most carbon-bearing species are seen together with a reduction of O_2 and H_2O. Willacy et al. (2002) find that the H I/H_2 ratio should be an observable measure of the mixing.

Grain freeze-out. Roberts & Herbst (2002) have recently presented new gas-grain chemical models for cold cloud cores, which simultaneously follows the chemistry that occurs in the gas and on grain surfaces. These models give results that strongly depart from pure gas-phase models at times greater than 10^5 years. The gas-phase and grain-surface chemistries are linked through accretion and desorption processes, based on new experimental results on the surface mobility of hydrogen atoms on olivine and amorphous carbon. Two sets of gas-grain models are considered, differing in the mobility of various atoms. Even though both accretion and desorption mechanisms act in these models, a steady-state chemistry is never reached. The abundances of many gas-phase species, including CO, H_2O, and O_2, rise until somewhere between $10^5 - 10^6$ years, at which time freeze-out begins to dominate and their abundances decline. With such behavior, molecules such as O_2, that takes a significantly long time to reach a high abundance in gas-phase models, are never able to reach this abundance in gas-grain models.

Although very promising, the gas-grain models do not optimally match all the observed constraints of well-known dark clouds at a single time. Pure gas-phase models with C/O=1 are able to match the observations fairly accurate at a single time. Explanations could be (1) differential desorption rates and (2) different chemical evolutionary times within a given cloud. There are some observational evidence for chemical variation across the dark cloud TMC-1 (e.g., Saito et al. 2002).

1.5 Molecules Far Away

Observations of the molecular gas component in distant galaxies enable us to study the conditions of star formation and the chemical evolution of objects at early epochs. Molecular gas has been detected in galaxies up to redshift $z = 4.7$ (Ohta et al. 1996; Omont et al. 1996), corresponding to a look-back time of almost 90% of the age of the Universe.

There are three sources of information about the molecular gas at high redshift: (1) H_2 in damped Lyα systems, (2) CO emission from far-infrared luminous galaxies and AGNs, and (3) molecular absorption-line systems at intermediate redshifts. Furthermore, molecules are believed to play an important role in formation of the very first generation of stars. This is due to the presence of H_2, HD, and LiH molecules in the primordial gas (e.g., Stancil, Lepp, & Dalgarno 1996, 1998; Galli & Palla 2002). Although the abundances of these primordial molecules are minute, they act as cooling agents of the primordial gas, and thereby allow the formation of stellar objects less massive than what is the case for a pure atomic gas.

Molecular hydrogen has been detected in a few damped Lyα systems (e.g., Petitjean, Srianand, & Ledoux 2000, 2002; Ledoux, Srianand, & Petitjean 2002), but with very low column densities, $N_{H_2} \le 10^{18}$ cm^{-2}. The H_2 seen in these system appears to originate in a warm (~3000 K) diffuse gas. This gas is not typical for the normal molecular ISM component found in galaxies.

Carbon monoxide, CO, has been detected in 15 galaxies above $z = 1$ (see Wiklind & Alloin 2002 for a recent compilation). The detected systems are all far-infrared luminous galaxies with elevated star formation rates. Most of the CO-detected objects are gravitationally lensed. The CO lines give information about the global properties of the molecular ISM, such as the overall mass and the average excitation conditions. It can also be used to derive the dynamical mass. If the commonly used conversion factor between CO integrated intensity and H_2 column density is used, many of these distant systems have a mass that is dominated by the molecular gas component. Due to the extreme weakness of the observed signal, in almost all cases only the CO lines are observable with present-day instrumentation. Apart from the global parameters, little can be learned about the chemical evolutionary state of these distant galaxies.

A few molecular absorption systems have been detected at redshifts $z = 0.25 - 0.89$ (e.g., Wiklind & Combes 1994; Combes & Wiklind 1999; Menten et al. 1999). These rare systems, where the line of sight to a background radio-loud QSO penetrates the inner region of an intervening galaxy, gives an unprecedented view of the molecular gas component in distant galaxies (see Fig. 1.3). Although only four such systems have been detected to date, 22 different molecular species have been observed, including several isotopic variants, and most molecules have been observed in at least two different transitions. These data give detailed information about the chemistry, the abundances, and the physical conditions in the molecular gas in these distant galaxies. Comparison with similar data from Galactic absorption-line studies and those of a few nearby galaxies shows no significant differences between the molecular gas properties (Fig. 1.4). This suggests that the star-forming conditions in distant galaxies are essentially the same as we find in local systems.

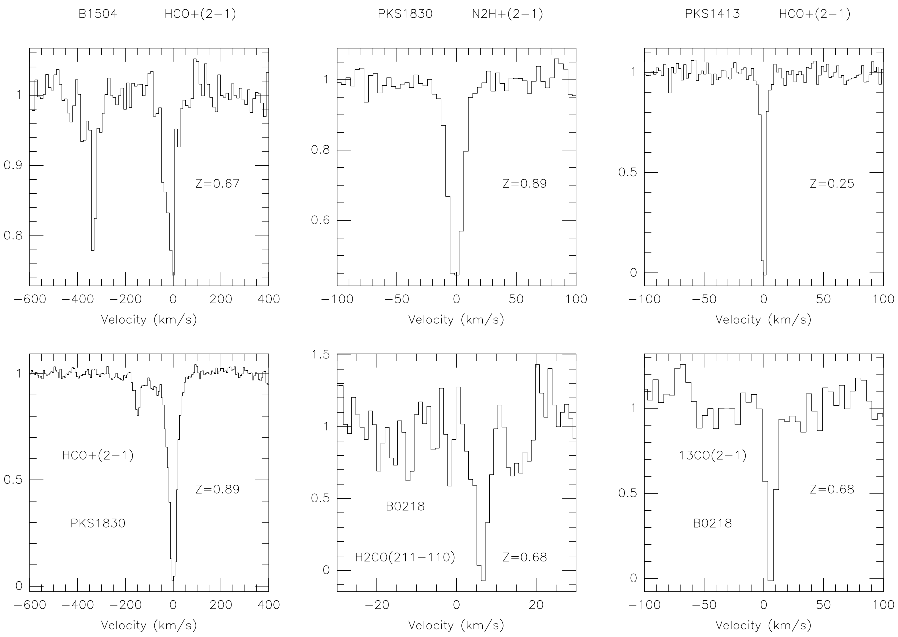

Fig. 1.3. Several different molecular transitions seen in absorption toward the four known molecular absorption-line systems at intermediate redshifts. (Adapted from Combes & Wiklind 1998.)

1.6 Challenges for the Future

Astrochemistry remains very much an active research area. This brief overview of molecules in the ISM can only point to some of the unsolved problems and their impact on our understanding of the physical and chemical processes related to the formation of stars and planetary systems. A non-exhaustive list of challenges for the future includes:

- A better physical understanding of the combined gas-phase and grain-phase chemistry in dark clouds, as well as the formation of molecular ices. This can possibly lead to an explanation of the low observed abundances of molecular oxygen and water vapor in dark clouds. It may also explain the elevated abundances of molecular species found through absorption-line studies of diffuse and translucent molecular gas.
- Molecular absorption-line observations of diffuse and translucent molecular clouds in the Milky Way show that the chemistry is very similar to that of dark clouds. This suggests that the interior of dark clouds may not be as "dark" as previously thought. The inhomogeneous structure of molecular gas needs to be investigated further. The possibility of very small-scale structure, as shown by recent reports, needs to be studied as well.
- In order to understand the physics of stellar formation it is necessary to construct self-consistent models combining gas- and grain-phase chemistry, hydrodynamical models of the protostellar cloud, and the full transfer of radiation. Small steps toward such models have been taken, but the fully consistent model is yet to be constructed.

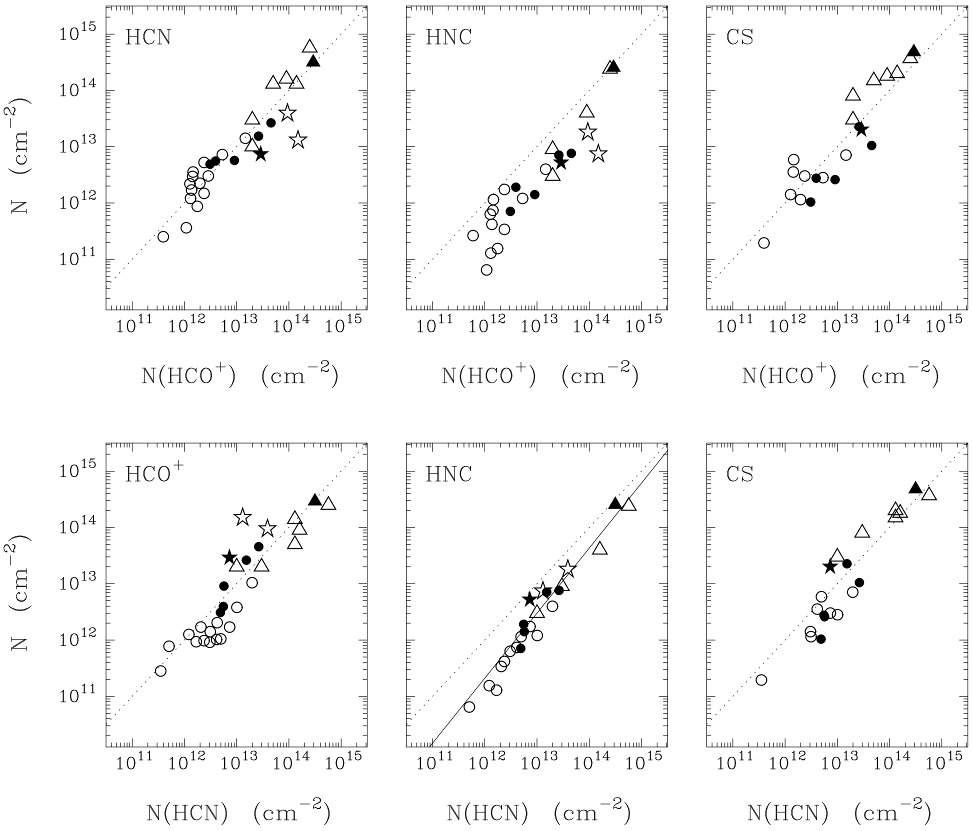

Fig. 1.4. The *top* panels show the column density of HCO^+ plotted versus column densities of HCN, HNC, and CS. The *bottom* panels show column density of HCN plotted versus column densities of HCO^+, HNC, and CS. Open circles represent Galactic diffuse clouds (Lucas & Liszt 1996), filled circles represent data from Cen A (Wiklind & Combes 1997a), open triangles absorption data toward Sgr B2 (Greaves & Nyman 1996), filled star absorption data for PKS 1413+135 at $z = 0.25$ (Wiklind & Combes 1997b), open stars B31504+377 at $z = 0.67$ (Wiklind & Combes 1996b), and the filled triangle PKS 1830–211 at $z = 0.89$ (Wiklind & Combes 1996a, 1998). The dashed line is a one-to-one correspondence between the column densities and not a fit to the data.

- Observations of molecules at high redshift allow not just a study of the global properties, but also of the detailed physical and chemical evolutionary status of the gas. Since the molecular gas is directly involved in the formation of new stars, these data give information on which processes are at work in these earlier epochs and if the star formation proceeds in the same manner as in nearby systems.

The future looks promising indeed for observations of molecules in the ISM, both in the Milky Way and in very distant galaxies. The Atacama Large Millimeter Array (ALMA) will increase the sensitivity at millimeter and submillimeter wavelengths by a factor 10–100 (depending on the wavelength regime). Paired with a similarly large increase in the angular resolving power, it will be able to do very sensitive observations of molecules on small

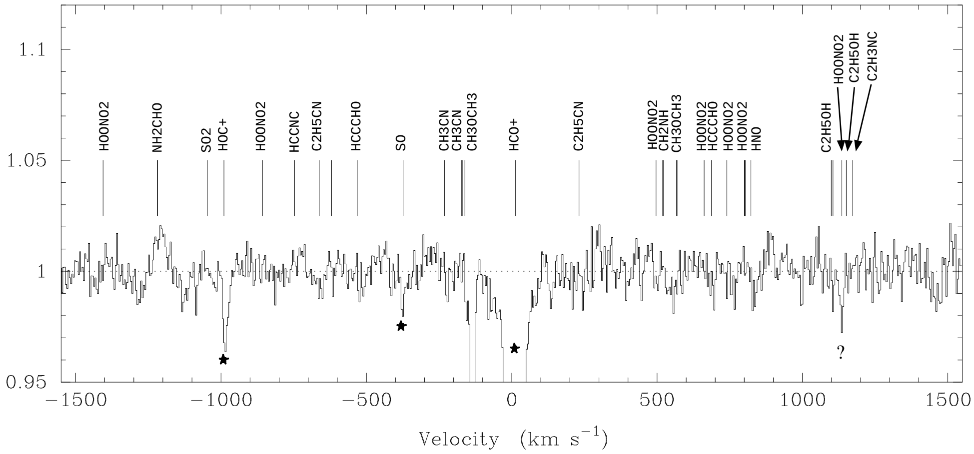

Fig. 1.5. Coadded observations from a monitoring project of the HCO^+(2-1) absorption line at $z = 0.89$ toward PKS 1830–211. The two deep absorption lines correspond to two lines of HCO^+(2-1). In addition a weak line of HOC^+(2-1) can be seen, as well as SO. This spectrum represents several tens of hours of total observing time with the 15 m SEST (Wiklind & Combes, unpublished). With ALMA a similar spectrum can be obtained in a matter of minutes.

spatial scales. This is likely to give insights into how protostars form and evolve, as well as allow studies of protoplanetary disks. The increased sensitivity will allow detailed studies of molecular absorption-line systems. An example of what can be achieved with ALMA in a few minutes of observing time, but which requires several days with present-day instruments, is shown in Figure 1.5. Here coadded spectra from a monitoring program of HCO^+(2-1) absorption at $z = 0.89$ toward PKS 1830–211 reveal the presence of the isomer HOC^+(2-1) as well as a line of sulphur monoxide, SO. The HOC^+ molecule has an abundance that is $\sim 2.6 \times 10^{-4}$ that of HCO^+, similar to values found in our Galaxy. Assuming Galactic abundance ratios for CO/H_2, the HOC^+/H_2 abundance ratio for the $z = 0.89$ system is $\sim 10^{-10}$.

On a shorter time scale, the new Atacama PAthfinder EXperiment (APEX) will put a single dish submillimeter telescope on Chanjantor at an altitude of 5000 m. This will allow observations up to the THz region (300 μm) and make it possible to observe for the first time the ground transitions of many light hydrides believed to exist and play an important role in the molecular chemistry.

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