Diffuse Atomic and Molecular Clouds

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Key Words

interstellar medium, interstellar molecules, spectroscopy

Abstract

Diffuse interstellar clouds have long been thought to be relatively devoid of molecules, because of their low densities and high radiation fields. However, in the past ten years or so, a plethora of polyatomic molecules have been observed in diffuse clouds, via their rotational, vibrational, and electronic transitions. In this review, we propose a new systematic classification method for the different types of interstellar clouds: diffuse atomic, diffuse molecular, translucent, and dense. We review the observations of molecules (both diatomic and polyatomic) in diffuse clouds and discuss how molecules can be utilized as indicators of the physical and chemical conditions within these clouds. We review the progress made in the modeling of the chemistry in these clouds, and the (significant) challenges that remain in this endeavor. We also review the evidence for the existence of very large molecules in diffuse clouds, and discuss a few specific clouds of particular interest.

1. INTRODUCTION

Given that the density of the diffuse interstellar medium is, on average, far lower than those of even the best laboratory vacuums, it was surprising to astronomers in the late 1930s to discover that molecules exist in space (see comments by Eddington 1926 and by Dalgarno 2000). Yet, beginning in the 1930s when high-resolution optical spectroscopy was pioneered at the Mount Wilson Observatory and at the Dominion Astrophysical Observatory, sharp absorption lines seen in the spectra of several distant stars were soon recognized as being caused by the diatomic molecules CN, CH, and CH$^+$ (Dunham 1937; Swings & Rosenfeld 1937; McKellar 1940; Douglas & Herzberg 1941; Adams 1941; for an overview of early work on interstellar molecules, see Feldman 2001). Today astronomers are aware of the existence of several additional diatomic molecules and a number of polyatomics in the diffuse interstellar medium (ISM)—and a host of as-yet unidentified very large species such as the carriers of the unidentified infrared bands (UIBs) and the carriers of the diffuse interstellar bands (DIBs), a large collection of optical absorption features that have been noted in interstellar spectra since the 1920s. Despite initial expectations to the contrary, the diffuse ISM is chemically rich.

To persist in the harsh environment of interstellar space, molecules must form at rates sufficient to counterbalance their destruction. Molecular destruction occurs primarily by direct photodissociation or predissociation, which is a two-step process in which the molecule is first photoexcited to an unstable state and then dissociates. The formation of small molecules is generally thought to occur via gas-phase two-body (usually ion-neutral) reactions, although grain surface reactions can also be important. It is also possible that some complex species are formed in red supergiant stellar outflows or through the destruction of solid dust grains that are shattered by shocks.

Interstellar molecules can be identified through their electronic, vibrational, and rotational spectra. Typically, electronic transitions of simple molecules arise in the ultraviolet (UV) or visible portion of the spectrum; vibrational bands lie at infrared (IR) wavelengths; and rotational lines are seen at radio wavelengths. Hence the study of interstellar molecules necessarily involves a wide range of observational techniques and instruments. Diffuse clouds are unique in that the same line of sight can, in principle, be observed by all of these techniques, providing a far broader understanding of the physical and chemical state of diffuse clouds than is possible for other cloud types.

In addition to gas-phase molecules, solid dust grains (which contain about 1% of the mass in diffuse clouds) play a very significant role in controlling the physics and chemistry. Some molecules are formed on dust grain surfaces, and in addition the absorption and scattering of starlight by dust controls the attenuation of starlight passing through interstellar clouds. Radiation (especially in the UV) plays a very strong role in governing the physical and chemical state of interstellar molecules; hence dust extinction is a crucial parameter in modeling the chemistry of diffuse clouds. For recent reviews of dust in the ISM, see Draine (2003), Whittet (2003), or Witt, Clayton & Draine (2004), each of which provides comprehensive discussions of dust observations, properties, and models.

2. THE CLASSIFICATION OF DIFFUSE CLOUDS

2.1. General Comments

Early models (e.g., McKee & Ostriker 1977) classified the ISM into three phases: the Cold Neutral Medium (CNM), often referred to as clouds; the Warm Ionized Medium or Warm Neutral Medium (WIM or WNM), which is sometimes considered the boundary layers of the CNM; and the Hot Ionized Medium (HIM), which is sometimes referred to as the intercloud medium or the coronal gas. These phases are thought to be in approximate pressure equilibrium with one another (see Savage & Sembach 1996 or Cox 2005 for a general description of the physical conditions and phases in the galactic ISM).

The CNM itself appears to contain a variety of cloud types, spanning a wide range of physical and chemical conditions. The densest clouds that are most protected from UV radiation from stars are variously referred to as dense clouds, dark clouds, or molecular clouds. The most tenuous clouds, fully exposed to starlight, are usually called diffuse clouds. Clouds that fall in between these two extremes are often referred to as translucent clouds. Unfortunately, the application of these categories has not been uniformly consistent in the literature; here we propose a new systematic classification for cloud types. Our proposed classifications are summarized in **Table 1**, and illustrated using a chemical model in **Figure 1**.

We wish to emphasize that the ISM is inherently complex in its structure, and though theorists and observers prefer to think of isolated, homogenous clouds, most real sightlines probably consist of a mixture of different types of clouds. In some cases, a sightline may consist of a concatenation of discrete clouds, whereas in other cases the gas may have an "onion-like" structure, with dense cloud material in the center, surrounded by translucent gas, which is in turn surrounded by more diffuse gas.

Because of this complexity, our classification of "cloud types" is intended to reflect the local conditions in a parcel of gas, rather than the overall properties of a larger structure. In particular, one must keep in mind that the definitions do not refer to line-of-sight properties. Although line-of-sight properties are the most easily observed ones, observational technology (especially the development of ultra-high resolution spectrographs) is now making it possible for astronomers to better estimate local properties (or, at least, the average properties of individual parcels of gas).

Table 1 Classification of Interstellar Cloud Types

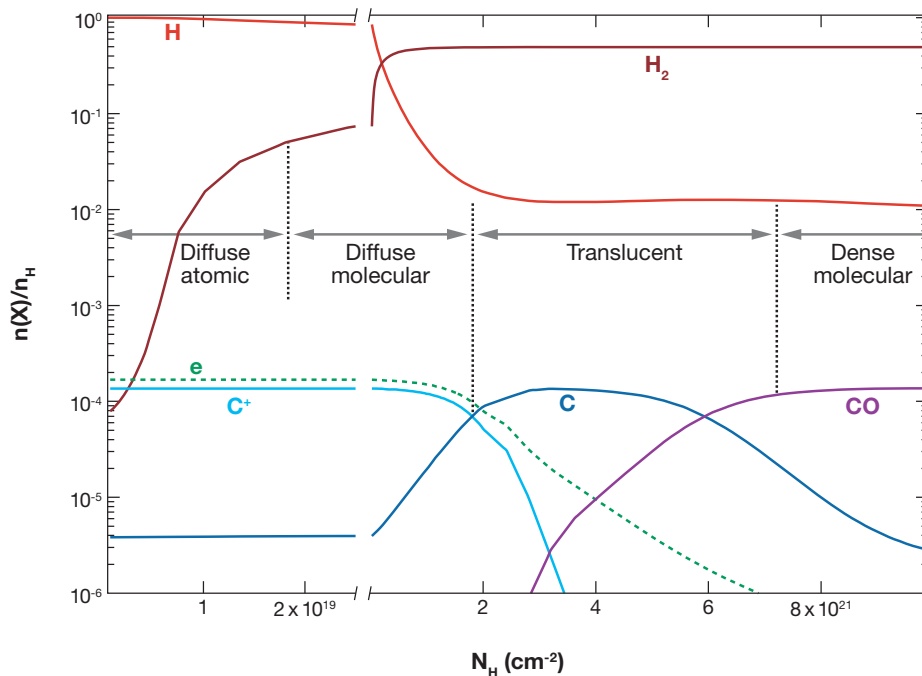|	Diffuse Atomic	Diffuse Molecular	Translucent	Dense Molecular
Defining Characteristic	$f^n_{H_2} < 0.1$	$f^n_{H_2} > 0.1$ $f^n_{C^+} > 0.5$	$f^n_{C^+} < 0.5$ $f^n_{CO} < 0.9$	$f^n_{CO} > 0.9$
A_V (min.)	0	~ 0.2	$\sim 1-2$	$\sim 5-10$
Typ. n_H (cm^{-3})	10–100	100–500	500–5000?	$>10^4$
Typ. T (K)	30–100	30–100	15–50?	10–50
Observational Techniques	UV/Vis H I 21-cm	UV/Vis IR abs mm abs	Vis (UV?) IR abs mm abs/em	IR abs mm em

Figure 1

Results from photodissociation region model [with $n_H = 100$ cm^{-3} and $\chi_{UV} = 1$] from Neufeld et al. (2005), illustrating the revised definitions of cloud types.

Our proposed classification of cloud types may be easily reconciled with the working definition that infrared astronomers sometimes use to designate "diffuse" versus "dense" sightlines. For an infrared astronomer, a line of sight showing no evidence of ice coatings on grains is considered "diffuse" even though the total visual extinction may be ten or more magnitudes. For instance, several lines of sight in Cygnus, such as the very well-studied clouds toward Cygnus OB2 12, have large total extinctions but are considered diffuse because they show no ices. In our view these sightlines may be interpreted simply as extended aggregations of diffuse atomic and/or diffuse molecular clouds as defined below.

2.2. Definitions of Key Quantities

There are a number of important quantities that are useful in describing lines of sight, and for classifying the nature of parcels of gas. To make our notation clear, we collect the definitions of these quantities here.

We define the local number density (in cm^{-3}) of a certain species X to be $n(X)$. The directly observable quantity is not the number density, but the column density (essentially the integral of the number density along the line of sight), which we denote $N(X)$. For a given atom Y, we define the total number density of its nuclei to be n_Y; for

example, $n_H = n(H) + 2n(H_2)$. For the case of carbon, most nuclei are in the form of C^+, C, or CO, so we can approximately write $n_C \approx n(C^+) + n(C) + n(CO)$. Similar expressions can be written in terms of column densities, e.g., $N_H = N(H) + 2N(H_2)$. The fraction of an atom's nuclei that are in a particular form is usually denoted as f_X (for example, the fraction of hydrogen in the form of H_2 is customarily denoted f_{H_2}). However, this notation is ambiguous because it can refer either to the local conditions or to a line-of-sight average. We define f^n to be the local fraction, in terms of number densities, and f^N to be the line-of-sight fraction, in terms of column densities. Thus, $f^n_{H_2} = 2n(H_2)/n_H$ and $f^N_{H_2} = 2N(H_2)/N_H$. Similarly, $f^n_{CO} = n(CO)/n_C$, etc.

Because hydrogen nuclei are by far the most abundant, the total amount of material along a line of sight can be approximated by N_H. Bohlin, Savage & Drake (1978) showed that there is a good correlation between N_H and the reddening E_{B-V}: In sightlines with $E_{B-V} < 0.5$, $N_H = 5.8 \times 10^{21}$ cm^{-2} mag$^{-1} \times E_{B-V}$. This relation was later extended up to $E_{B-V} \sim 1$ by Rachford et al. (2002). Although the quantity E_{B-V} is easier to determine observationally (by simply comparing the apparent color of the background star to the expected color based on its spectral type), the total visual extinction A_V is more commonly used as a stand-in for N_H. For the remainder of this review, we assume that $R_V \equiv A_V/E_{B-V} \sim 3$, so that $N_H \sim 1.7 \times 10^{21}$ cm^{-2} mag$^{-1} \times A_V$, and consider only A_V.

2.3. Diffuse Atomic Clouds

Diffuse atomic clouds represent the regime in the ISM that is fully exposed to the interstellar radiation field, and consequently nearly all molecules are quickly destroyed by photodissociation. Hydrogen is mainly in neutral atomic form, and atoms with ionization potentials less than that of hydrogen (most notably carbon) are almost fully ionized, providing abundant electrons. The paucity of molecules implies that very little chemistry occurs in this gas. Mysteriously, these clouds seem to be where most of the diffuse interstellar band carriers (see Section 6.2) thrive.

Many sightlines with low extinction seem to pass exclusively through diffuse atomic gas. Such sightlines typically have N_H less than about 5×10^{20} cm^{-2}, and are sufficiently optically thin to be observable by means of visible and UV absorption-line measurements. Diffuse atomic clouds typically have a fairly low density ($\sim$10–100 cm^{-3}), and temperatures of 30–100 K. We again wish to emphasize that the defining characteristic of these clouds is the low molecular fraction ($f^n_{H_2} < 0.1$), not the overall line-of-sight properties or the density. However, in sightlines that only cross diffuse atomic clouds, $f^N_{H_2}$ will also be <0.1.

2.4. Diffuse Molecular Clouds

Diffuse molecular clouds represent the regime where the interstellar radiation field is sufficiently attenuated, at least at the individual wavelengths that dissociate H_2, that the local fraction of hydrogen in molecular form, $f^n_{H_2}$ becomes substantial (>0.1). However, enough interstellar radiation is still present to photoionize any atomic carbon, or to photodissociate CO, such that carbon is predominantly still in the form of C^+ ($f^n_{C^+} > 0.5$).

In steady state, diffuse molecular clouds must necessarily be surrounded by diffuse atomic gas, in order to provide the shielding of radiation. This means that most sightlines that cross a diffuse molecular cloud will also cross diffuse atomic gas. [One exception is the sightline toward HD 62542; see Section 7.2.1.] Therefore, one has to be careful in interpreting line-of-sight quantities such as $f^N_{H_2}$, which will always be lower than the $f^n_{H_2}$ within the diffuse molecular cloud. For example, even a cloud that is fully molecular inside ($f^n_{H_2} = 1$) is likely to be along a line of sight with $f^N_{H_2}$ considerably less than unity.

The presence of abundant H_2 in diffuse molecular clouds permits chemistry to begin in earnest. Molecules are observed in these clouds in absorption in the UV/visible (e.g., CO, CH, CN, C_2, C_3), in the infrared (CO, H_3^+), and at millimeter wavelengths (e.g., HCO^+, OH, C_2H). These clouds typically have densities on the order of 100–500 cm^{-3}, and temperatures that range from 30–100 K.

Diffuse molecular clouds can be observed in sightlines with a wide range of visual extinction, or total hydrogen column density. The lower limit of N_H where molecular hydrogen begins to shield itself from interstellar radiation is a few times 10^{20} cm^{-2}, or $A_V \sim 0.2$.

2.5. Translucent Clouds

With sufficient protection from interstellar radiation, carbon begins to transition from ionized atomic form into neutral atomic (C) or molecular (CO) form. To call attention to this transition, van Dishoeck & Black (1989) defined such material as "translucent clouds." The chemistry in this regime is qualitatively different than in the diffuse molecular clouds, both because of the decreasing electron fraction and because of the abundance of the highly reactive C atoms. Although the original definition was cast in terms of isolated cloud structures with a certain range of A_V, van Dishoeck (1998) expanded the definition to be more general, in order to encompass gas on the periphery of dense molecular clouds, for example.

In many ways, the translucent cloud regime is the least well understood of all the cloud types. This is partly because of a relative lack of observational data, but also because theoretical models do not all agree on the chemical behavior in this transition region. In some models, there is a zone where the abundance of C exceeds that of C^+ and CO; in others the peak abundance of C falls below that of C^+ and CO. To cope with this uncertainty, we propose a working definition of translucent cloud material as gas with $f^n_{C^+} < 0.5$ and $f^n_{CO} < 0.9$. This definition reflects the fact that C^+ is no longer the dominant form of carbon as it converts to neutral or molecular form, but also excludes the dense molecular clouds, where carbon is almost exclusively CO. We stress that this working definition may need to be changed as better observational and/or theoretical understanding of these clouds is achieved.

Translucent cloud material must, in steady state, be surrounded by diffuse molecular cloud material, and is not expected to be present for sightlines with A_V less than about unity, because of the insufficient shielding of radiation. Thus, sightlines with $A_V > 1$ are candidates for hosting translucent clouds. However, a high value of A_V alone does not imply the presence of translucent material, as it could represent simply

a pile-up of diffuse molecular clouds along the line of sight (e.g., Cygnus OB2 12). Once again, it is the local parameters that define this cloud type. Such high extinction sightlines are still observable with optical absorption line techniques, and can be observed at millimeter wavelengths in both absorption and emission. In the UV, increasing extinction makes observations very difficult. As discussed in Section 3.1 below, it has not yet been possible to observe (at UV wavelengths) sightlines that are clearly dominated by translucent clouds.

A series of papers by Gredel, van Dishoeck, Black and others have sought to study translucent clouds through high-resolution optical studies of CH and CN together with mm-wave observations of CO (Gredel et al. 1992, 1994; van Dishoeck et al. 1991). This work has led to at least two cases where translucent clouds seem to be present (HD 169454, Jannuzi et al. 1988; and HD 210121, Gredel et al. 1992).

2.6. Dense Molecular Clouds

With increasing extinction, carbon becomes almost completely molecular ($f^n_{CO} \sim 1$), defining the regime of dense molecular clouds. The chemistry is again qualitatively different, as the electron abundance is very low (cosmic-ray ionization being the dominant source) and the reactive C is replaced by the very stable CO. This regime is entered only in sightlines with $A_V > 5$–10; again, not all such sightlines will contain dense cloud material, and if dense cloud material is present it is likely to be surrounded by translucent material.

These clouds are typically self-gravitating, and are most often observed by IR absorption and mm-wave emission methods. Their densities are typically at least 10^4 cm^{-3}, and their kinetic temperatures are typically on the order of 10–50 K in the quiescent regions. There is a very rich literature on dense cloud chemistry, both from observational and theoretical perspectives. In fact, the earliest chemical models were focused on these environments (e.g., the seminal papers by Solomon & Klemperer 1972, Herbst & Klemperer 1973, and Watson 1973). Most of the more than 130 currently known interstellar molecules were found through observations of microwave rotational transitions in such clouds, starting with the discovery of OH by Weinreb et al. (1963), followed by a host of other new detections such as CO, NH_3, H_2O, and H_2CO (for an early review of radio-wavelength interstellar molecular observations, see Rank et al. 1971).

Much of the recent work on dense clouds has been directed toward hot cloud cores where star formation is incipient (for a recent paper summarizing the current state of modeling of such clouds, see Smith et al. 2004). We do not further discuss dense clouds in this review.

3. OBSERVATIONS OF MOLECULES IN DIFFUSE CLOUDS

3.1. The Most Abundant Molecule: H_2

Molecular hydrogen has always been expected to be abundant in diffuse clouds (e.g., Eddington 1937; Strömgren 1939; Hollenbach et al. 1971) but because it is symmetric

and homonuclear, it possesses no electric-dipole allowed vibrational or rotational transitions. Therefore, the only probes of H_2 in the diffuse ISM are the far-UV electronic transitions in the Lyman and Werner bands lying below 1115 Å (Spitzer & Zabriskie 1959).

Observing these transitions was not possible until the advent of space-based far-UV spectrographs. The first success, using rocket-based spectroscopy, was by Carruthers (1970), who detected strong H_2 absorption in the line of sight toward ξ Persei. In 1972, the *Copernicus* orbital observatory was launched, with the primary scientific goal of observing interstellar H_2 absorption (Rogerson et al. 1973). *Copernicus* detected molecular hydrogen in more than 100 sightlines with A_V less than about 1.5. *Copernicus* H_2 surveys can be found in Spitzer et al. (1973) and Spitzer, Cochran & Hirshfeld (1974). An extensive review of H_2 studies based on *Copernicus* observations can be found in Shull & Beckwith (1982). The essential results of the *Copernicus* H_2 surveys were: (*a*) in the observed sightlines, $f^N_{H_2}$ ranged from nearly 0 to about 0.6, with a discontinuous transition from $<10^{-4}$ up to >0.01 at about $N_H \approx 5 \times 10^{20}$ cm^{-2} (Spitzer et al. 1973; Savage et al. 1977); (*b*) significant rotational excitation in the ground electronic and vibrational state was detected everywhere, as discussed in Section 4.2 below.

The *Far Ultraviolet Spectroscopic Explorer* (FUSE) observatory (launched in 1999 and still in operation at this writing; Moos et al. 2000) provides spectra over a broader far-UV wavelength region than *Copernicus*, with similar spectral resolving power and far greater sensitivity, thus allowing the detection and analysis of H_2 toward much dimmer stars (see **Figure 2**). FUSE has allowed the detection and analysis of molecular hydrogen in a wide range of environments not accessible to *Copernicus*, such as high galactic latitude clouds formed in the halo of the Milky Way (Shull et al. 2000; Richter et al. 2001), the Magellanic Clouds (Tumlinson et al. 2002), and more heavily reddened diffuse cloud sightlines (Snow et al. 2000; Rachford et al. 2001, 2002). The general findings of the FUSE H_2 surveys are consistent with those from *Copernicus*, but have extended them into new regimes.

The highest line-of-sight molecular fraction measured with FUSE is $f^N_{H_2} \sim 0.8$, for the line of sight toward X Persei (aka HD 24534), a diffuse cloud with one of the richest molecular contents yet found (Lien 1984; Sheffer et al. 2002b). Rachford et al. (2001, 2002) searched for evidence of translucent clouds in highly reddened sightlines, but failed to identify any line of sight that seems convincingly dominated by a translucent cloud. Rachford et al. concluded that, up to $A_V \approx 3$, most lines of sight consist of a summation of multiple diffuse clouds, each with a low to moderate hydrogen molecular fraction, but none containing purely molecular hydrogen or purely neutral and molecular carbon. The inability of FUSE to detect translucent clouds should not be taken as evidence that such clouds do not exist; rather, it is a reflection of the fact that it cannot observe stars lying behind clouds with large extinction ($A_V > 3$), and that it has relatively low spectral resolution.

Some absorption lines of vibrationally excited H_2 lie in the mid-UV, and have been studied with spectrographs [Goddard High Resolution Spectrograph (GHRS), and Space Telescope Imaging Spectrograph (STIS)] on the *Hubble Space Telescope* (HST). The first detection was toward ζ Oph (Federman et al. 1995). Subsequently, Meyer
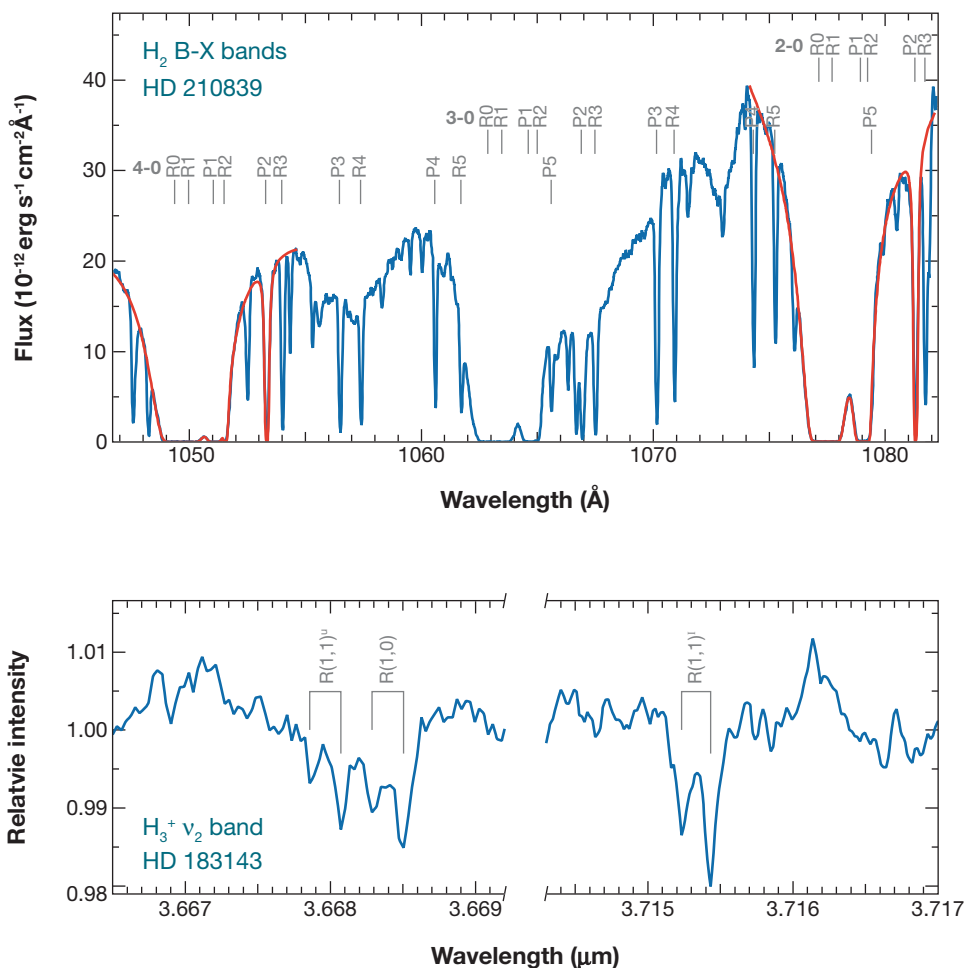
Figure 2

(*Top*) Spectrum of H_2 obtained with *Far Ultraviolet Spectroscopic Explorer* (FUSE) and model fit in red (adapted from Rachford et al. 2002); (*bottom*) spectrum of H_3^+ (adapted from McCall et al. 2002).

et al. (2001) found a rich spectrum of absorption lines from vibrationally excited H_2 toward the star HD 37903, which is the exciting star in the reflection nebula NGC 2023. Meyer et al. also detected vibrationally excited H_2 toward three other stars (HD 37021, HD 37061, and HD 147888). More recently Boissé et al. (2005) have detected absorption from vibrationally excited H_2 toward HD 34078, another star embedded in circumstellar gas, also finding lines arising from rotational levels as high as $J = 11$ of the ground electronic and vibrational state. The mechanisms for populating H_2 in such highly excited states is discussed in Section 4.2 below.

3.2. HD in Diffuse Clouds

The H_2 isotopomer HD was first detected in *Copernicus* spectra by Spitzer et al. (1973) and Morton (1975), and has subsequently been observed in many sightlines by FUSE. The HD lines arising from the lowest-lying rotational levels ($J = 0$ and $J = 1$) are far weaker than their counterparts for H_2, but are in many cases still strong enough to be saturated, requiring a curve-of-growth analysis for column density determinations. To date, HD analyses from FUSE spectra have been published only for a few stars (Ferlet et al. 2000; Lacour et al. 2005) though undoubtedly many more detections reside in the FUSE archives. In addition, Lacour et al. have reanalyzed *Copernicus* spectra for several stars, resulting in a uniform survey of HD abundances in some 17 sightlines.

The ratio of HD to H_2—more specifically, $N(HD)/2N(H_2)$—in the Lacour et al. survey ranges from a few times 10^{-7} to several times 10^{-6}. This is somewhat higher than the values found earlier from *Copernicus* data, but those values were based on two strong lines that were saturated.

It would be useful if the HD/H_2 ratio were a reliable indicator of the atomic ratio D/H, because the latter is an important indicator of the early expansion rate of the universe and therefore valuable in cosmology (e.g., Schramm & Turner 1998; Olive, Steigman & Walker 2000). But for three distinct reasons the comparison of HD to H_2 is difficult to apply to the cosmological problem.

First, in diffuse molecular clouds where H_2 is self-shielding (see Section 5.2.1) the far-UV lines of HD remain optically thin, or at best only marginally saturated, and therefore HD is not self-shielded. This favors H_2 and leads to a reduced HD/H_2 ratio, smaller than the atomic D/H value. Second, the lower mobility of D atoms on grains as compared to H atoms greatly reduces the formation rate of HD as compared to H_2, again acting to reduce the HD/H_2 ratio relative to the H/D ratio. But third, HD has a gas-phase formation channel, through the "chemical fractionation" reaction $H_2 + D^+ \rightarrow HD + H^+$ (Ferlet et al. 2000), which tends to enhance the HD/H_2 ratio and depends on the cosmic-ray ionization rate (Black & Dalgarno 1973).

As noted by Ferlet et al. (2000), if HD column densities reach the level where the molecule becomes self-shielding, then HD becomes the dominant reservoir of deuterium, and the HD/H_2 ratio would reflect the overall D/H value. So far, no observed HD column densities have come close to the level where self-shielding would occur, and in general we conclude that the HD/H_2 ratio is not useful for determining the cosmological D/H ratio, although it may be useful in constraining the rate of cosmic-ray ionization (which produces D^+).

3.3. Heavier Diatomics in Diffuse Clouds

3.3.1. Carbon monoxide.
In addition to electronic transitions in the UV, CO possesses (unlike H_2) dipole-allowed rotational transitions in the mm-wave band and vibrational transitions in the infrared. Because the electronic transitions are the strongest, the most sensitive searches for CO in diffuse clouds have been performed in the UV, but CO has been detected in diffuse clouds by the other methods as well.

In the radio, both emission and absorption lines of CO have been detected in diffuse clouds. Direct comparisons of CO and H_2 can be made if radio CO emission

is observed in the same sightlines as far-UV H_2 absorption. Such comparisons are risky due to the differing regions that are sampled, but assignment of the mm-wave emission to the same clouds that produce the H_2 absorption can be made on the basis of velocity matches. Knapp & Jura (1976), Kopp et al. (1996), and Liszt (1997) have made such comparisons, generally finding a CO/H_2 ratio of about 10^{-6}, consistent with expectations based on diffuse cloud gas-phase chemistry models.

A few detections of the CO fundamental vibrational band near 4.6 μm have been reported for diffuse clouds on the basis of ground-based observations (McCall et al. 1998; Shuping et al. 1999). For the most part IR studies of CO gas-phase absorption have been applied to dense clouds and not diffuse regions—but with improved spectral resolving power and sensitivity, further pursuit of the IR gas-phase absorption in diffuse clouds might be profitable (especially given the current lack of any UV instruments capable of observing the electronic bands).

The first UV detection of CO was made toward ζ Ophiuchi, using a rocket-borne spectrograph (Smith & Stecher 1971). Several far-UV bands of CO were subsequently detected by *Copernicus* observers in a number of sightlines (Jenkins et al. 1973; Morton 1975; Snow 1975; Smith, Stecher & Krishna Swamy 1978; Wannier, Penzias & Jenkins 1982).

In principle, UV absorption line measurements should be most useful for comparing CO and H_2, because the exact same pathlength can be probed using both molecules. However, early attempts to derive CO abundances using *Copernicus* were hampered by uncertainties surrounding the oscillator strengths for the transitions, difficulties in resolving the rotational structure within each electronic band, and saturation effects. The oscillator strength issues were largely resolved by the systematic compilations of Morton & Noreau (1994) and Eidelsberg et al. (2004 and references cited therein). Better resolution of rotational structure became possible with GHRS and later STIS on HST, yielding column density determinations impacted only by saturation effects (e.g., Sheffer et al. 1992; Lambert et al. 1994; Wannier et al. 1999; Kaczmarczyk 2000a,b).

The issue of line saturation can be avoided by observing the weak intersystem bands of CO in the UV, which are usually unsaturated even in sightlines with high total column densities. The difficulty in analyzing these transitions, which involve perturbations between electronic states, lies in a lack of accurate laboratory wavelengths and f-values. For some time, results from studies of these intersystem bands appeared to be inconsistent with those based on the allowed electronic transitions, but using a combination of theory and observations, Sheffer et al. (2002a) were able to determine consistent empirical f-values for some seven intersystem bands of CO and apply them to the determination of the CO column density and excitation in the line of sight toward ζ Ophiuchi. In parallel with this work, laboratory studies of the intersystem bands yielded oscillator strengths consistent with the astronomically derived values (Eidelsberg et al. 2004). Very recently, P. Sonnentrucker, D. Welty, J. Thorburn & D. York (submitted) have taken advantage of the revised f-values for the intersystem bands of CO to conduct a survey of several lines of sight where other diatomics such as H_2, C_2, and CN are also measured, finding that CO correlates more strongly with CN than with H_2, and that current

models underestimate the amount of CO present in diffuse molecular clouds. The close correspondence between CO and CN has also been discussed by Pan et al. (2005).

Because the HST no longer has any UV spectroscopic capability (although several observations reside in its archives), CO observations are now being conducted in the far-UV using FUSE. The first such study, by Sheffer et al. (2003), reports the detection of 11 Rydberg bands of CO toward the star HD 203374A. Because the FUSE spectral resolving power is insufficient to separate the rotational lines within the bands, Sheffer et al. made use of high-resolution optical data on CH and UV data on the longer-wavelength CO bands (from STIS) to determine the line-of-sight velocity structure and hence the accurate column density of CO. They were then able to calculate empirical f-values for the far-UV lines. Their most significant result was that the far-UV transitions that are not blocked by strong H_2 absorption have higher f-values than previously believed, which means that these transitions contribute more strongly to the predissociation of CO than in standard models, though this is offset by enhanced self-shielding.

The ratio of ^{12}CO to ^{13}CO is an indicator of the isotopic ratio of carbon, of interest for galactic nucleosynthesis studies. In principle, lines from the different isotopic species can be observed, and the isotopic ratio determined, from observations in the UV, IR, or radio. However, the determination of the isotopic ratio is complicated by selective photodissociation (when ^{12}CO self-shields, ^{13}CO is more easily destroyed), saturation corrections (^{12}CO lines have larger optical depth), and chemical fractionation (which enhances ^{13}CO; Sheffer et al. 2002b). Federman et al. (2003) discuss these processes in more detail, and present UV observations with the HST/GHRS that suggest that the value of $^{12}CO/^{13}CO$ toward two sightlines in Ophiuchus is $\sim$120, higher than the terrestrial value of 90.

The carbon monoxide oxygen isotopic ratios ($C^{16}O/C^{17}O$ and $C^{16}O/C^{18}O$) have also been derived from UV observations, and are larger than the corresponding overall isotope ratios in local interstellar gas (Sheffer, Lambert & Federman 2002b). Sheffer et al. explain this as being caused by the favored photodestruction of $C^{17}O$ and $C^{18}O$ relative to $C^{16}O$, which is more self-shielded.

3.3.2. Other diatomics seen at UV/optical wavelengths.
The first three interstellar molecules ever detected, CH, CH^+, and CN (see Section 1), were diatomics, but detection of additional diatomics has generally been a challenge, as most species fall well below H_2, CO, CH, CH^+, and CN in abundance.

After extensive early searches and initial detections made only with some difficulty (Souza & Lutz 1977, 1978; Snow 1978), diatomic carbon is now routinely observed with high-S/N high-resolution spectrographs on large telescopes (Hobbs, Black & van Dishoeck 1983; van Dishoeck & de Zeeuw 1984; van Dishoeck & Black 1986a; Lambert, Sheffer & Federman 1995; Thorburn et al. 2003). The Phillips band system of C_2, which has several bands in the far red and near-IR, has proven most readily observable. The first detection, by Souza & Lutz (1977), was of the (1,0) band near 1.014 μm toward the highly reddened distant B star Cygnus OB2 12 (see Section 2.1), while most subsequent work has been focused on the (3,0) and especially the (2,0)

bands (at 7720 and 8765 Å, respectively). The fundamental (0,0) band of C_2 near 1.2 μm has not, to our knowledge, been detected.

Because C_2 is a homonuclear diatomic, there are no allowed dipole transitions between rotational levels of the ground state, and many rotational levels are populated. Rotational lines arising from levels up to $J = 12$ or higher are typically observed. As discussed in Section 4.4, the rotational excitation of C_2 is a useful indicator of the local radiation field intensity and gas density, as these levels are populated by both radiative and collisional pumping, as in the case of H_2 (van Dishoeck & Black 1982).

The first molecule detected through radio observations, the OH radical, also has electronic transitions at 1222 Å and 3078 Å. The far-UV line was detected by Snow (1976a) using the *Copernicus* satellite, whereas the near-UV line was first detected from the ground, with great effort due to atmospheric ozone interference (Crutcher & Watson 1976a; Chaffee & Lutz 1977; Felenbok & Roueff 1996; Federman, Weber & Lambert 1996). The near-UV OH features are more easily observed from space, though the transition lies near the long-wavelength cut-off for instruments such as the *International Ultraviolet Explorer* (IUE) and the HST—and was not covered at all by *Copernicus* or FUSE. Though the OH $\lambda3078$ feature was readily detectable with the GHRS and the STIS, only a few observations have been reported (e.g., Snow et al. 1994). Microwave absorption due to OH in diffuse sightlines was observed by several researchers, as summarized by Crutcher (1979) and Liszt & Lucas (1996). Based on both the optical and the radio observations, the column densities of OH, at the level of 10^{-8} of the total hydrogen, are generally consistent with gas-phase chemistry models for diffuse clouds (e.g., Black & Dalgarno 1977, van Dishoeck & Black 1986b).

Another hydride, NH, has an electronic transition at 3358 Å, which is accessible from the ground, but proved to be very difficult to detect. Gas-phase chemistry models show no rapid reaction sequence leading to NH, so a detection would suggest that some other process, such as grain surface formation, must be responsible. The first intensive search for NH was negative (Crutcher & Watson 1976b), consistent with gas-phase chemistry, but eventually NH was detected (Meyer & Roth 1991) at a level suggesting either that current models are overlooking important gas-phase reactions or that grain surface formation may be important even in diffuse clouds (Crawford & Williams 1997). Recently, D.E. Welty (private communication) has detected NH in an additional three sightlines (HD 62542, HD 73882, and Walker 67).

Another diatomic not expected to be abundant according to gas-phase models is N_2, which has electronic transitions only in the far-UV. An early search based on *Copernicus* data proved negative (Lutz, Owen & Snow 1979), but recently Knauth et al. (2004) have claimed a detection toward HD 124314 and have reported an additional detection toward 20 Aquilae (D. Knauth; private communication), based on FUSE spectra in both cases. Because of blending with interstellar H_2 lines, blending with a prominent stellar photospheric line, and the possibility of contamination by N_2 in the upper atmosphere, it is very difficult to conclude unambiguously that interstellar N_2 has been detected. But, as discussed by Snow (2004), Knauth et al. have addressed these issues and make a convincing case for detection. The inferred column density of N_2 in the sightlines where the detections are claimed is higher than expected from

gas-phase models for diffuse clouds, but lower than expected for dense molecular clouds, suggesting that dust grain surface reactions may be responsible. In view of the observational complexities, clearly it is important to search for N_2 in additional lines of sight, and Knauth and colleagues are doing so, again using FUSE.

Jura (1974), followed by Dalgarno et al. (1974), realized that ionized chlorine can undergo rapid reactions with H_2 to form HCl^+, which then leads to H_2Cl^+ and HCl (through electron-ion recombination). Jura predicted that HCl might be detectable through an electronic transition at 1291 Å, but this line was not detected in a subsequent search using *Copernicus* data (Jura & York 1978). The idea lay dormant for some time, until Federman et al. (1995), using HST/GHRS spectra, detected HCl absorption toward ζ Oph. The detected column density was consistent with the predictions of models.

3.3.3. Diatomics seen in the millimeter-wave.
Many molecules, diatomics and larger, have dipole-allowed transitions in the mm-wave spectral region, suggesting that radio observations of molecular emission and absorption from diffuse clouds, in combination with UV, optical, and IR absorption measures, could provide detailed information on the chemistry of these clouds. Radio observations have the significant advantage that velocity components are resolved and that many more species are accessible than at optical and UV wavelengths. In practice there are difficulties, as diffuse clouds have lower molecular column densities than the dense clouds typically observed at radio frequencies, and mm-wave emission can arise from an extended region rather than solely from the pencil beam where the observed absorption lines arise. Important efforts to combine radio and optical data on specific diffuse clouds have been carried out by Crutcher (1985) and Gredel et al. (1994).

Such difficulties are eliminated when performing absorption measurements at millimeter waves; however, there are relatively few suitable continuum sources in our galaxy. Liszt & Lucas (2002, and references cited therein) have pioneered the use of extragalactic radio emitters, in particular AGN/blazars, as continuum sources against which to measure mm-wave absorption lines. A major advantage of using extragalactic background sources is that they randomly sample the ISM, as opposed to OB stars, which are often directly associated with concentrations of interstellar matter.

The result of their work is that a significant heritage of radio absorption-line detections has been compiled for diffuse clouds. Among the diatomics detected in diffuse clouds are CO (both emission and absorption; Liszt & Lucas 1998), CH (emission; Liszt & Lucas 2002), CN (absorption; Liszt & Lucas 2001), and OH (emission and absorption; Liszt & Lucas 1996, Liszt 1997). Other diatomics found in absorption include the sulfur-bearing species CS, and SO (Lucas & Liszt 2002) as well as SiO (Lucas & Liszt 2000a).

3.4. Triatomic and Polyatomic Molecules in Diffuse Clouds

Given that gas-phase chemistry can form abundant diatomic molecules in diffuse clouds, a few polyatomics are expected as well, according to models (e.g., van Dishoeck & Black 1986b). Polyatomics in diffuse clouds took much longer to find than

diatomics, but a combination of optical absorption measurements, IR detections of vibrational transitions, and millimeter-wave radio absorption and emission observations has recently revealed a surprisingly rich chemistry in these clouds.

3.4.1. H_3^+ in diffuse clouds.

The most fundamental polyatomic molecule is the ion H_3^+, whose presence was predicted originally by Martin, McDaniel & Meeks (1961) in regions where H_2 is partially ionized, formed through the reaction

$$H_2^+ + H_2 \rightarrow H_3^+ + H.$$
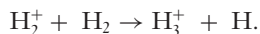
Once formed, H_3^+ can donate its extra proton to just about any atom or molecule, thereby initiating a network of ion-molecule reactions that is thought to be responsible for the formation of many interstellar molecules. For a detailed review of the chemistry of, and the search for, interstellar H_3^+, see Geballe (2000).

Initially it was thought that H_3^+ would be important only in dense clouds, where H_2 is dominant and ionization is provided by cosmic rays, and so the first searches were aimed at dark molecular clouds with embedded protostars that could be used as infrared continuum sources. Because H_3^+ has no tightly-bound excited electronic states, there are no detectable spectral features in the visible or UV; and because H_3^+ has no permanent dipole moment, it has no allowed rotational transitions either. The only spectroscopic probe of this molecule, therefore, is a set of ro-vibrational lines between 3.5 and 4.0 μm. Meaningful searches for these transitions required accurate frequencies, which were determined experimentally by Oka (1980), and f-values, which were computed by J. K. G. Watson (private communication).

Geballe & Oka (1996) finally detected H_3^+ toward two deeply embedded protostars (W33A and GL2136), and this momentous discovery was followed by several additional detections in dense clouds (McCall et al. 1999, Brittain et al. 2004). Though significant quantities of H_3^+ were not expected in diffuse clouds, this species was soon detected in several diffuse sightlines (McCall et al. 1998, 2002, Geballe et al. 1999; see **Figure 2**). One of the first detections of H_3^+ in a classical diffuse cloud was made recently (McCall et al. 2003) toward the star ζ Persei, which has visual extinction $A_v \approx 1$ mag.

The discovery of H_3^+ in diffuse lines of sight was quite surprising, and the abundance of H_3^+ in diffuse clouds remains a challenge to understand (Section 5.4.2).

3.4.2. Triatomics observed via optical absorption.

Triatomic carbon, C_3, was long expected to exist in diffuse clouds, but proved to be elusive for a time. The strong electronic band of C_3, near 4050 Å, appears in many cometary emission spectra, and given its high f-value appeared to be the best choice for interstellar absorption searches. After some failed searches (Clegg & Lambert 1982; Snow, Seab & Joseph 1988), Haffner & Meyer (1995) reported a tentative detection in the line of sight toward HD 147889 in the ρ Ophiuchi cloud. Subsequently the first clear-cut detection was made by Maier et al. (2001), who found C_3 absorption in three diffuse clouds (ζ Ophiuchi, 20 Aquilae, and ζ Persei). More recently, some 15 detections of interstellar C_3 have been reported by Oka et al. (2003), using the Apache Point Observatory

(APO) 3.5-m telescope. The resolving power of the APO spectra was insufficient for resolving the individual rotational lines, but then Ádámkovics, Blake, & McCall (2003) obtained much higher-resolution spectra of C_3 in 10 sightlines and were able to extract the rotational excitation (see Section 4.4).

H_2O and CO_2 have been sought through UV absorption in diffuse clouds without success. Snow (1975) and Snow & Smith (1981) used *Copernicus* to search for water vapor in the line of sight toward ζ Ophiuchi, with no detections—though the latter search revealed a tentative feature at the right wavelength that might have represented a marginal detection. However, Spaans et al. (1998) conducted an intensive search for the 1240 Å transition of H_2O toward HD 154368, placing a limit on the column density of 9×10^{12} cm^{-2}, or about 10^{-8} times the total hydrogen column density, which is more stringent than the *Copernicus* limit for ζ Oph.

In the case of CO_2, upper limits for electronic transitions in the far UV were reported by Snow (1980) based on *Copernicus* spectra, though the reported limit was not sensitive enough to strongly challenge gas-phase chemistry models, which do not predict much CO_2 in any case.

Tentative detections of CH_2 have been reported by Lyu et al. (2001) based on HST/GHRS spectra of HD 154368 and ζ Ophiuchi; if the detections are real, they correspond to abundances of CH_2 in good agreement with predictions of gas-phase chemical models.

3.4.3. Polyatomics seen in millimeter-wave absorption. As mentioned in Section 3.3.3 above, detections of millimeter-wave absorption are extraordinarily useful because absorption (as opposed to emission) measurements necessarily apply to exactly the same interstellar column that is studied via infrared, optical, and UV absorption-line observations, thus allowing a truly multispectral analysis of the chemistry in a given line of sight. Liszt & Lucas (2002, and references therein) have conducted extensive surveys of millimeter-wave absorption lines using extragalactic continuum sources.

The remarkable result of the millimeter-wave absorption line work is that many polyatomic species, including notably HCO^+, are detected in absorption along diffuse sightlines over a range of galactic latitudes (Liszt & Lucas 1994, 1996, Hogerheijde et al. 1995). Other polyatomic species detected in absorption include HCN (Lucas & Liszt 1994), H_2CO (Liszt & Lucas 1995), C_2H and C_3H_2 (Cox, Guesten & Henkel 1988; Lucas & Liszt 2000b), H_2S and HCS^+ (Lucas & Liszt 2002), NH_3 (Liszt, Lucas, & Pety 2006), and HOC^+ (Liszt, Lucas & Black 2004); several others were sought and not detected (see **Table 3**).

Some of the extragalactic continuum sources observed by Liszt & Lucas are also bright enough at visible wavelengths for optical interstellar line measurements with large telescopes. Tappe (2004) and Tappe & Black (2004; and A. Tappe & J. H. Black, in preparation) have taken advantage of this opportunity to compare the radio and optical data to develop a more complete picture of the observed diffuse clouds and their physical and chemical states, and found a very good correspondence between the optical and millimeter-wave absorption components. This work conclusively demonstrates that these extragalactic sightlines pass through the same types of diffuse clouds
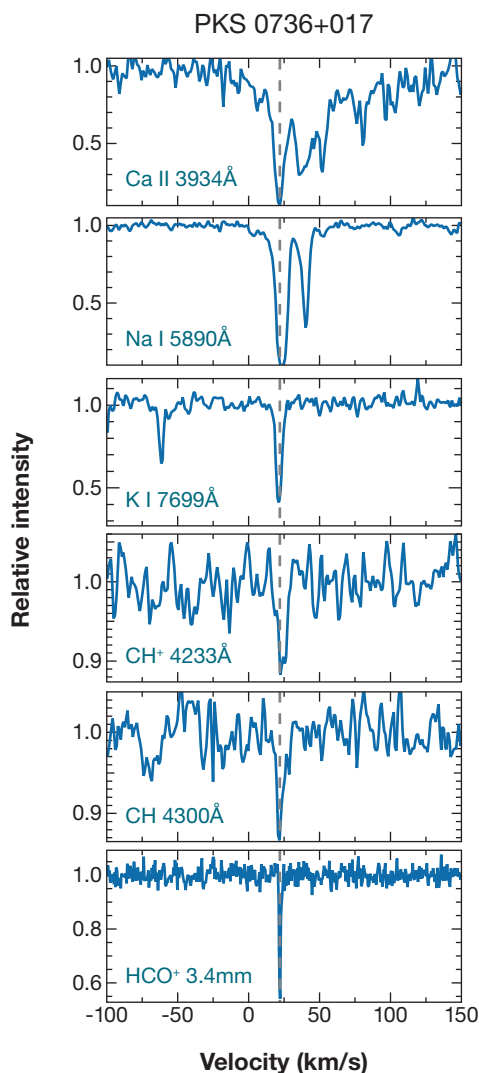
Figure 3

Comparison of optical and millimeter-wave spectra of PKS 0736 + 017, adapted from Tappe (2004). The HCO^+ data are from Lucas & Liszt (1996).

that are usually studied in absorption at optical and UV wavelengths against OB stars. **Figure 3** shows the comparison of optical and millimeter-wave absorption lines toward the source PKS 0736 + 017. Taken together with the Lucas & Liszt surveys, it is now clear that the chemistry of polyatomic molecules in diffuse clouds is surprisingly rich. Clearly, much work is left to be done to fully understand these observations; as an initial step, Tappe (2004) has explored the question of whether the observations support a connection between CH^+ and the formation of HCO^+.

4. MOLECULES AS INDICATORS OF CLOUD PHYSICAL CONDITIONS

In the diffuse ISM, most molecules exist in their ground electronic and vibrational states. The population of the various rotational states is generally controlled by both collisional and radiative processes. Collisions with atoms and other molecules (especially H and H_2) can cause either rotational excitation or de-excitation. For molecules with dipole moments (and hence, allowed rotational transitions), excitation can occur by stimulated absorption in the cosmic microwave background (CMB), and de-excitation can occur by spontaneous emission and by stimulated emission. Molecules without dipole moments can still be excited by radiation, by absorbing photons in an electronic transition. If all of the relevant molecular processes are understood, the observed rotational excitation can provide valuable information about the physical conditions in a cloud, such as the density, kinetic temperature, and the intensity of the radiation field.

4.1. CN and the Cosmic Microwave Background

The CN radical was one of the first interstellar molecules to be detected, and immediately its rotational excitation was noted by McKellar (1940, 1941), who estimated the excitation temperature of CN to be about 2.3 K. Some have cited this as a "pre-discovery" of the CMB (e.g., Feldman 2001), though McKellar apparently did not speculate that the excitation might be caused by a pervasive radiation field.

The rotational excitation of CN remained unexplained until 1965, when the CMB was discovered (Penzias & Wilson 1965, Dicke et al. 1965). It was soon realized that the excess excitation of CN could be explained by radiative equilibrium with the CMB (Field & Hitchcock 1966, Thaddeus & Clauser 1966)—and this was, in fact, the first definitive measurement of the temperature of the CMB (a temperature of about 2.6 K was the consensus interpretation at the time; see the review by Thaddeus 1972). A much more precise determination of the excitation temperature of CN in several sightlines has been presented by Roth & Meyer (1995), who also provide a useful review of previous observations.

Of course more recent measurements from above Earth's atmosphere have provided a more direct measure of the temperature of the CMB (Fixsen & Mather 2002), but it is noteworthy that a simple analysis of the rotational excitation of a diatomic interstellar molecule revealed the essential result well before the more sophisticated direct measurements of the CMB spectrum were possible.

4.2. Rotational Excitation of H_2: A Case of UV Pumping

As a homonuclear molecule with no dipole-allowed vibrational or rotational transitions, molecular hydrogen is a premier indicator of physical conditions in diffuse interstellar clouds. Far-UV observations with *Copernicus* and FUSE show that in most diffuse clouds there is a substantial population of H_2 in rotational levels up to about $J = 6$, and that the relative populations can usually be interpreted in terms of two
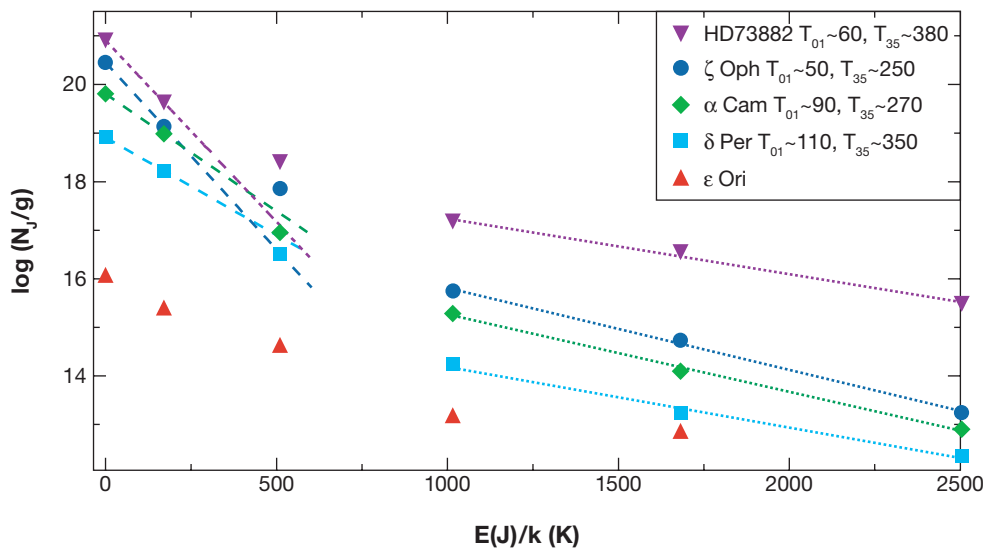
Figure 4

Boltzmann diagram of H_2 in five diffuse cloud sightlines, illustrating the low T_{01} and higher T_{35}. Column densities from Spitzer et al. (1973), Spitzer, Cochran & Hirshfeld (1974), and Snow et al. (2000).

distinct excitation temperatures. As illustrated in **Figure 4**, the relative populations of the low-lying levels ($J = 0$ and $J = 1$, in particular) generally correspond to a temperature of 50 to 150 K with a mean around 80 K, whereas the higher-J levels fit a temperature of a few to several hundred Kelvin (Spitzer et al. 1973; Spitzer & Cochran 1973; Spitzer, Cochran & Hirshfeld 1974; Spitzer & Zweibel 1974; Savage et al. 1977; Rachford et al. 2002; Browning et al. 2003).

The temperature derived from the $J = 0$ and $J = 1$ levels of H_2 (T_{01}) is generally assumed to represent the kinetic temperature (T_{kin}) of the gas, because the lines arising from these states are usually saturated and therefore self-shielding, making radiative pumping out of these states relatively inefficient. However, for T_{01} to be rigorously equal to the T_{kin}, the balance between $J = 0$ and $J = 1$ would have to be dominated by collisional transitions. The real situation is more complex, because $J = 0$ and $J = 1$ belong to different nuclear spin configurations (para and ortho, respectively) and cannot interconvert through ordinary collisions, but only via reactive collisions with H^+ or H_3^+, or by collisions with paramagnetic grains. Although the rate of such reactive collisions may well be sufficient to ensure that $T_{01} = T_{kin}$, the complexity of the situation should not be forgotten.

Black & Dalgarno (1973) proposed that the high-J excitation was the result of radiative pumping, in which absorption of UV photons was followed by a cascade back to excited vibrational and rotational levels of the ground electronic state. This mechanism was mentioned by Spitzer & Cochran (1973), among others, and was later modeled by Spitzer & Zweibel (1974) and Jura (1975a,b; see also Black & Dalgarno

1977; Black, Hartquist & Dalgarno 1978; Federman Glassgold & Kwan 1979). The analysis of the relative populations of the high-J levels can provide information about the radiation field, the density, and perhaps also the distribution of rotational levels populated when H_2 is initially formed. More recently, the excitation of H_2 has been modeled in great detail by many researchers using improved cross sections, and taking into account the effects of vibrational excitation (e.g., Browning, Tumlinson & Shull 2003, and references therein).

The early *Copernicus* results indicated that the high-J lines in most diffuse cloud sightlines are formed in environments with radiation fields much more intense than the average interstellar field. Several *Copernicus*-based studies (references cited above) led to the conclusion that the material where the excited H_2 resides is close to a source of UV radiation, presumably the hot star that is being observed. Velocity studies of the high-J lines seemed to support this notion, because several cases were found where the absorption lines arising from excited levels showed negative velocities, as if they were formed in gas expanding away from the star. The spectral resolving power of *Copernicus* was only marginally sufficient for such a conclusion, however, and higher-resolution studies by Jenkins et al. (1989) and Jenkins & Peimbert (1997) did not show such a trend.

As mentioned in Section 3.1, a few cases have been found where an observable fraction of the H_2 exists in excited vibrational levels of the ground electronic state. The first detection, by Federman et al. (1995) was toward ζ Ophiuchi, and suggested that the UV radiation field pumping the H_2 was not much higher than the average interstellar value (in contrast to the *Copernicus* results with rotationally excited H_2). However, observations of vibrationally excited H_2 by Meyer et al. (2001) toward HD 37903 and by Boissé et al. (2005) toward HD 34078 have demonstrated a close interaction between the molecular gas and the radiation fields of these particular stars.

FUSE data have yet to be fully exploited for studies of the high-J lines in more heavily-reddened lines of sight than those analyzed by Browning et al. (2003). At least one individual case has been well studied, that of HD 185418 (Sonnentrucker et al. 2003), but no general survey of rotational excitation toward reddened stars has yet been completed, though one is under way (B. Rachford, private communication). For HD 185418, Sonnentrucker et al. show that the excited H_2 is widely distributed and not concentrated near the star where the UV radiation field is intense, suggesting instead that the high-J lines in this case may be populated collisionally in a warm neutral gas, an idea previously proposed by Gry et al. (2002) for other sightlines.

4.3. An Intermediate Case: CO

The rather small dipole moment (0.1 Debye) of CO implies that it is less efficient than, say, CN at relaxing rotational excitation through spontaneous emission. Therefore, CO does not reach equilibrium with the CMB like CN. On the other hand, the fact that CO does have a nonzero dipole moment implies that it will not reach equilibrium with the kinetic temperature of the gas via collisions, because spontaneous emission does have some effect. The critical density (the density at which the collisional de-excitation rate equals the spontaneous emission rate) for the $J = 1$–0 transition of CO

is around 1000 cm^{-3}, so only at densities higher than this would thermal equilibrium be reached.

Consequently, one would expect the rotational excitation temperature of CO, at the densities of diffuse clouds, to be somewhere in between the CMB temperature (2.7 K) and the kinetic temperature of the gas ($\sim$50 K). Observationally, the CO rotational excitation temperature is typically 5 to 15 K (Smith et al. 1978, Lambert et al. 1994, Shuping et al. 1999, Sonnentrucker et al. 2003). The observed rotational excitation can be used to infer the gas density and temperature. Detailed models for CO excitation have been presented by Goldsmith (1972), van Dishoeck & Black (1987), Lyu, Smith & Bruhweiler (1994), and Warin, Benayoun & Viala (1996), among others.

4.4. Excitation Analysis of C_2 and C_3

As homonuclear symmetric molecules, both C_2 and C_3 lack permanent dipole moments, so neither can quickly relax radiatively from excited rotational levels of the ground electronic and vibrational state. Hence the excitation levels of both of these molecules can be interpreted to provide information on both the collisional temperature (from the low-lying rotational populations) and the presence and nature of extrathermal excitation mechanisms (from the higher-J states).

The interpretation of C_2 excitation is very similar to the results of H_2 rotational analysis as described above. One advantage over the H_2-based studies is that the absorption lines of C_2 are almost always optically thin and unsaturated (see **Figure 5**),
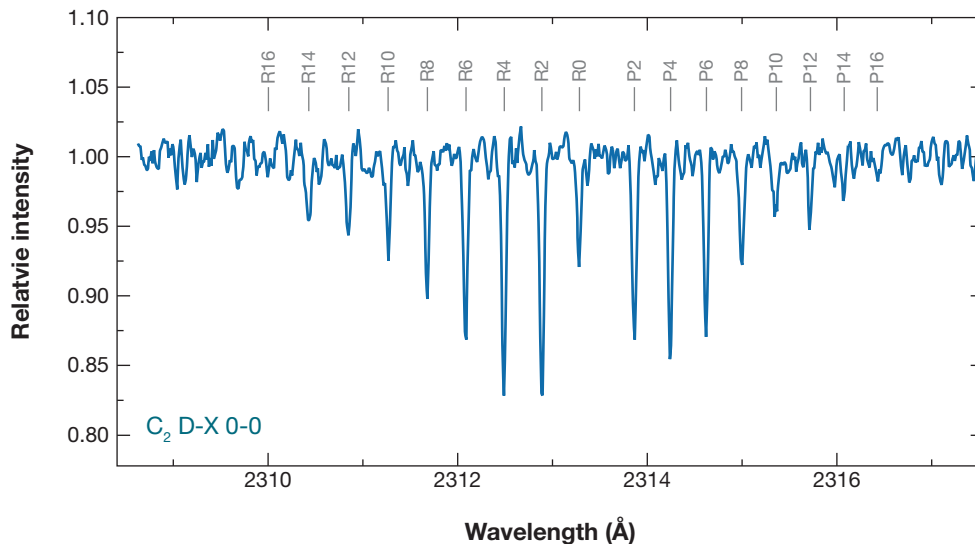

Figure 5

Spectrum of the Mulliken band of C_2 toward X Per (HD 24534), adapted from P. Sonnentrucker, D. Welty, J. Thorburn & D. York (submitted).

which simplifies the derivation of the relative rotational populations (saturation effects hamper the analysis of some H_2 high-J lines, especially in sightlines with significant reddening and large H_2 column densities). Because the energy separations among rotational levels in C_2 are smaller than in H_2, many more levels are observed (up to J = 14 in some cases), adding to the precision of the analysis. The C_2 excitation is also sensitive to a different portion of the radiation field, because the pumping occurs mainly through the Phillips band system near 1 μm rather than in the UV (as in H_2). The use of C_2 as an indicator of diffuse cloud physical conditions was modeled in detail by van Dishoeck & Black (1982). One of us (B.J.M.) has used this model to construct a calculator that derives values of both n and T from equivalent widths of C_2 lines; this calculator is available online at dibdata.org. The temperatures derived from C_2 are generally consistent with T_{01} of H_2, within the mutual uncertainties; for example, toward ζ Persei, $T(C_2) = 80 \pm 15$ K and $T_{01} = 58 \pm 8$ K, and toward o Persei, $T(C_2) = 60 \pm 20$ K and $T_{01} = 48 \pm 5$ K.

The spectrum of C_3 is more complicated, and Ádámkovics, Blake & McCall (2003) developed a novel method for obtaining rotational populations from spectra containing closely-spaced lines up to J = 30. As in the cases of H_2 and C_2, the low-J levels of C_3 are populated by collisions while the upper states show evidence of extrathermal excitation, which is most likely due to radiative pumping. Very good agreement with the earlier C_2 results was found for the inferred gas kinetic temperature, so the assumption of collisional equilibrium for the low-J states appears sound. But understanding the excitation of the high-J states requires detailed modeling. Roueff et al. (2002) carried out a detailed analysis of C_3 excitation in four lines of sight (including HD 210121; see Section 7.2.3 of this review), but have not yet published the details of their method.

5. CHEMICAL MODELS OF DIFFUSE CLOUDS

5.1. Physical and Chemical Processes

Most of the physical and chemical processes that occur in diffuse clouds are the same ones that operate in dense clouds; the major qualitative difference between these two types of clouds is that photoprocesses play an important role in diffuse cloud chemistry, whereas in dense clouds the large dust extinction suppresses them. The chemistry of diffuse and dense clouds has been reviewed by van Dishoeck (1998).

In terms of the heating and cooling balance of clouds, photons provide the dominant heating force in diffuse clouds via the photoelectric effect on dust, which injects relatively hot electrons into the gas. In terms of the ionization, abundant photons with energies >11.26 eV will photoionize nearly all of the carbon atoms in diffuse clouds, leaving a substantial fractional ionization $n(e)/n_H \sim 10^{-4}$, which is orders of magnitude higher than in dense clouds. Finally, in terms of chemistry, photodissociation substantially reduces the abundance of molecules, for example $H_2 + h\nu \rightarrow H + H$ or $CH + h\nu \rightarrow C + H$.

Aside from photon-induced reactions, much of the chemistry of diffuse clouds can be explained in terms of the gas-phase processes that occur in dense clouds. These

processes include ion-molecule reactions (e.g., $CH_2^+ + H_2 \rightarrow CH_3^+ + H$), which typically proceed with a Langevin rate coefficient of $\sim 10^{-9}$ cm^3 s^{-1}; dissociative recombination with electrons (e.g., $H_3^+ + e^- \rightarrow H + H + H$), which typically have faster rate coefficients of $\sim 10^{-7}$ cm^3 s^{-1}; radiative association reactions, which can be very slow (e.g., $C^+ + H_2 \rightarrow CH_2^+ + h\nu$, k $\sim 10^{-16}$ cm^3 s^{-1}) or quite fast (e.g., $C^+ + C_4 \rightarrow C_5^+ + h\nu$, k $\sim 10^{-9}$ cm^3 s^{-1}) depending on the size of the reactants; and charge exchange reactions (e.g., $H^+ + O \rightarrow O^+ + H$, which is endothermic by only 227 K). Neutral-neutral reactions involving radicals (e.g., $CH + O \rightarrow CO + H$) probably also play an important role, but we have less information about their rate coefficients, which have only recently become the subject of sustained experimental efforts. Finally, collisions with cosmic rays (high energy bare nuclei produced in supernovae) are very important in ionizing atoms and molecules with high ionization potentials, especially H, He, and H_2.

The role of interstellar dust grains is perhaps the most uncertain of all. It is clear that H_2 is produced abundantly on grains, by H atoms sticking to grains, tunneling between different binding sites, and eventually combining to form H_2, which is ejected from the grain by its large enthalpy of formation. This reaction is critically important, as gas-phase formation mechanisms for H_2 are incredibly slow. [However, in the early universe before heavy elements and solid dust existed, H_2 must have formed in the gas phase, probably by associative detachment of H with H^-; McDowell 1961, Dalgarno & McCray 1973; see also the very recent summary by Glover et al. 2006].

It is still an open question whether grain surface production in diffuse clouds is efficient only for H_2 (because H atoms tunnel easily and H_2 has such a low freezing point), or whether other molecules can be efficiently synthesized through grain chemistry and returned to the gas phase. van Dishoeck (1998) has suggested that the low observed column density of NH may provide an upper limit on the formation rate of molecules other than H_2 on grains. If other grain-surface reactions prove to be important, this could revolutionize our understanding of diffuse cloud chemistry. One additional grain "reaction" that seems to be very important (Lepp et al. 1988, Liszt 2003, Wolfire et al. 2003) is the neutralization of atomic ions by grains or large molecules (e.g., $H^+ + grain \rightarrow H + grain^+$), which proceeds much more efficiently than gas-phase radiative recombination (e.g., $H^+ + e^- \rightarrow H + h\nu$).

5.2. Key Transitions in Diffuse Clouds

To a first approximation, the chemical conditions in a parcel of gas are determined by the state of hydrogen and carbon. If hydrogen is ionized (H^+), as in the hot ionized medium, essentially no chemistry occurs. If hydrogen is neutral and completely atomic (H), as in diffuse atomic clouds, a limited chemistry can occur but the efficient ion-molecule reactions are deprived of their best reagent, H_2. When hydrogen becomes molecular (H_2), as in diffuse molecular, translucent, and dense molecular clouds, chemistry becomes more effective. Within this realm, the state of carbon plays a determining role: if carbon is photoionized (C^+), as in diffuse molecular clouds, there are abundant electrons available to destroy molecular ions through dissociative recombination, and ion-molecule chemistry is partially quenched. As carbon begins

to transition into the form of C or CO, in translucent clouds, the presence of the reactive C radical drives a more active chemistry. Once carbon becomes completely molecular (CO), as in dense clouds, electrons become much scarcer, and a rich ion-molecule chemistry can thrive.

5.2.1. The hydrogen transition. Within diffuse clouds, the state of (neutral) hydrogen is determined by the interplay of two processes: the production of H_2 from H atoms on grain surfaces, and the destruction of H_2 following absorption of photons. The rate of H_2 formation can be written (Hollenbach, Werner & Salpeter 1971) as $R_G = (1/2)\gamma\langle v_H\rangle n_g n(H)\langle\sigma_g\rangle$, where γ is the fraction of atoms striking a grain that eventually forms a molecule, $\langle v_H\rangle$ is the average velocity of H atoms, n_g and $n(H)$ are the number density of grains and H atoms, and $\langle\sigma_g\rangle$ is the mean cross-section of a grain. It is typically assumed (without evidence to the contrary) that γ and $\langle\sigma_g\rangle$ are independent of location in a cloud, and that $n_g \propto n_H$. With these assumptions, the H_2 formation rate scales as $T^{1/2}\, n_H\, n(H)$. Note that H_2 formation may not be as simple as these assumptions suggest (Biham et al. 2001, Cazaux & Tielens 2004).

The destruction of H_2 by photons in diffuse clouds is not a direct process, because the threshold for direct photodissociation is 14.7 eV. Instead, H_2 absorbs line photons in the Lyman (B-X) bands, inducing transitions from the ground state into various vibrational levels in the $B\,^1\Pi_u^+$ electronic state; these transitions have a certain probability of being followed by radiative decays into unbound dissociative (v > 14) levels of the electronic ground state. The Werner (C-X) bands make a substantially smaller contribution to dissociation (Spitzer 1978). The rate of H_2 destruction then depends only on the number density of H_2 molecules and on the radiation flux in the discrete transitions of the Lyman band. In the inner regions of a cloud, this radiation flux is attenuated by all of the H_2 molecules in the outer regions of the cloud, leading to a "self-shielding" of the H_2.

Models suggest that the transition to self-shielding is a fairly sharp one: Once a critical column density of H_2 has been built up, the fraction of hydrogen in the form of H_2 rises dramatically. This effect is seen in observations of H and H_2 by *Copernicus* (Savage et al. 1977): In sightlines with E(B-V) > 0.08 (corresponding to $N_H > 5 \times 10^{20}$ cm^{-2}), the column density of H_2 always exceeds 10^{19} cm^{-2}, whereas for E(B-V) <0.08, there is a wide range in H_2 column densities, presumably reflecting variations in number density in different sightlines. Models (e.g., van Dishoeck & Black 1986b) predict that even in the central regions of diffuse clouds with n $\sim$ 100 cm^{-3} a substantial fraction ($\sim$1/4) of hydrogen remains in atomic form. In clouds with densities $\sim$1000 cm^{-3}, the atomic hydrogen fraction declines to <1% (van Dishoeck & Black 1988).

5.2.2. The carbon transition. Roughly speaking, the state of carbon in diffuse clouds is determined by processes involving CO. In dense molecular clouds, nearly all carbon is in the form of CO, due to its chemical stability; that this is not the case in diffuse clouds is owing to the effect of photodissociation. CO is formed primarily following the reaction $C^+ + OH \rightarrow CO^+ + H$. When CO^+ is formed, it reacts with H_2 to form HCO^+, which then recombines with an electron to form CO. The

OH necessary for CO formation is formed following the slightly endothermic charge exchange between O and H^+ (formed by cosmic-ray ionization of H), followed by reactions of O^+ with H_2 to form OH^+, H_2O^+, and H_3O^+, followed by dissociative recombination. Other channels that may be important are the reaction of H_3^+ with O, and the neutral-neutral reaction of CH with O.

The major destruction pathway of CO is photodissociation. Much like the case of H_2, there are no pathways for direct photodissociation of CO at wavelengths longer than 912 Å. Unlike H_2, CO is destroyed by discrete absorptions into predissociated electronically excited states (which are quasi-bound with a finite lifetime). There are over 30 predissociated bands lying to the red of 912 Å (van Dishoeck & Black 1988, Viala et al. 1988), making the problem more complicated than in the case of H_2. With increasing depth into a diffuse cloud, the photodissociation rate will be reduced by self-shielding, and also by shielding by coincident lines of H and H_2.

The state of carbon results from the competition between production of CO by ion-neutral (and perhaps neutral-neutral) reactions and the (depth-dependent) destruction of CO by photons. Diffuse atomic and diffuse molecular clouds contain relatively little CO (it is all photodissociated to O and C, which is then photoionized to C^+). In translucent clouds, photoionization becomes less efficient and many models suggest a zone where carbon is predominantly in neutral atomic form (C). With sufficient depth (e.g., leading into a dense cloud) CO will become the dominant form of carbon. Once C or CO becomes dominant, the C^+ abundance drops by orders of magnitude. The chemical impact of this transition is profound, as it also results in a drop in the electron fraction and the removal of dissociative recombination as an important process in destroying molecular ions.

The exact location of the transition from C^+ to CO depends not only on A_V, but also on the number density, the strength and spectrum of the incident radiation field, and other parameters. According to the models of van Dishoeck & Black (1988) and Jannuzi et al. (1988), the cross-over point where $n(C^+) \sim n(CO)$ occurs at $A_V \sim 0.6$, or $N_H \sim 10^{21}$ cm^{-2} for clouds with $n_H \sim 700$ cm^{-3}. The C^+/CO transition is much less sharp than the H/H_2 transition, according to these models. Newer models (e.g., Neufeld et al. 2005) show a transition from C^+ to C around $A_V \sim 1$, and a distinct transition from C to CO around $A_V \sim 3$. Given the sensitivity of this transition to model parameters, these differences are not too surprising. However, the earlier models also used a too-low H_3^+ dissociative recombination rate coefficient, and adopted higher densities to fit the observed properties of specific clouds. Also, the newer models include the effect of C^+ recombination with large molecules (M.G. Wolfire, private communication).

5.3. Chemical Models

To our knowledge, a "complete" model of a diffuse cloud—that is, one where the complete physical and chemical structure is solved self-consistently—has not yet been attempted. Such a model would require treating the equations of hydrostatic equilibrium, thermal balance, radiative transfer, ionization balance, and chemical processes. In the following subsections we briefly discuss the models that have been

constructed that treat some subset of these equations. Before doing so, we wish to note that a great number of publications have considered a small subset of the chemistry [e.g., CH and CH$^+$ chemistry; Federman (1982)]; while these have led to a much better understanding of parts of diffuse cloud chemistry, we focus here on more comprehensive numerical models. We also wish to direct the reader's attention to the model of Turner (2000), which considers the chemistry in both diffuse and dense clouds, with a focus on molecules observed at radio wavelengths.

5.3.1. Early models. The first comprehensive model of a diffuse cloud was reported by Glassgold & Langer (1974). In many ways, this model comes close to the "complete" model discussed above, in that it utilizes pressure, thermal, electrical, and chemical balance equations. Like most of the models that would follow, it is a one-dimensional model, and assumes steady state (that the formation rate for each species equals its destruction rate). It does not make an assumption for the total number density, but instead treats it as a free parameter, subject to pressure balance with an assumed external pressure. This model's greatest shortcoming is the very small set of species considered; it only explicitly treats the atoms H, He, C, and Ca (along with their ions) and the molecules H_2, H_2^+, and H_3^+. The same researchers (Glassgold & Langer 1975) later considered the transition of C$^+$ to CO, but not in the context of their comprehensive model.

A much more complete treatment of the chemistry was given by Black & Dalgarno (1977) and Black, Hartquist & Dalgarno (1978); their models included at least 18 atoms and more than 30 molecules. They modeled a diffuse cloud as consisting of two regions (a "cold core" and a "warm envelope") with constant number density and temperature, and varied these parameters (while maintaining pressure balance) to best fit the observed abundances of atomic and molecular species in clouds toward ζ Ophiuchi and ζ Persei.

5.3.2. van Dishoeck & Black models. The next major advance in diffuse cloud modeling came nearly a decade later, in a paper aptly entitled "Comprehensive Models of Diffuse Interstellar Clouds: Physical Conditions and Molecular Abundances" (van Dishoeck & Black 1986b), in which improved models are compared with the sightlines toward ζ Ophiuchi, χ Ophiuchi, ζ Persei, and o Persei. These models utilized a somewhat larger chemical network (schematic diagrams of the chemistry are given in their figures 4–8), improved the treatment of radiative transfer in the H_2 lines, and also computed the rotational excitation of H_2, C_2, and CO. Furthermore, these models assumed hydrostatic equilibrium, including the gravitational potential of the gas, yielding continuous density gradients through the clouds. One drawback of these models is that thermal balance was not explicitly treated, but instead polytropic equations of state were assumed. This work indeed represents the most comprehensive modeling of diffuse clouds that had been done at the time, and it has not yet been surpassed in the completeness of its treatment by subsequent models. One unfortunate feature of these models is that they adopted a value for the H_3^+ dissociative recombination rate that is about three orders of magnitude too small (this value was in fashion at the time of these models).

Subsequently, these models were extended to denser sightlines with higher visual extinctions, referred to by the researchers as "translucent" clouds. This work began with two models of the HD 169454 sightline (Jannuzi et al. 1988), and was then extended to even higher densities and visual extinctions along with an improved treatment of the photodissociation of CO (van Dishoeck & Black 1988). Direct comparisons to the HD 29647 and HD 147889 clouds were also made (van Dishoeck & Black 1989).

5.3.3. Meudon models. An ongoing program of modeling of diffuse clouds has been conducted in Meudon, beginning with the work of Viala (1986). This model, which assumes a constant number density and temperature, was applied to ζ Ophiuchi (Viala, Roueff & Abgrall 1988) and later to ζ Persei (Heck et al. 1993). Subsequent work has focused on the possible role of turbulence (e.g., Falgarone et al. 1995) or shocks (e.g., Flower & Pineau des Forets 1998) to explain the anomalous abundance of CH^+ (discussed below). The models were also extended by Le Bourlot et al. (1993) to treat dense photodissociation regions (PDRs), using a variety of isochoric, isobaric, and self-gravitating models. More details of the model, including the incorporation of deuterium chemistry, have been given by Le Petit et al. (2002). The "Meudon PDR model" has very recently been applied to the classical diffuse cloud toward ζ Persei (Le Petit et al. 2004), in an effort to understand the large observed column density of H_3^+ in that sightline (McCall et al. 2003), and has also been applied to the case of HD 34078 (Boissé et al. 2005); the application of this model to diffuse clouds is reviewed in Le Petit et al. (2006).

5.3.4. Cloudy model. An emerging development in this field is the recent application of the workhorse spectral synthesis code Cloudy (reviewed in Ferland 2003) to diffuse clouds. Shaw et al. (2006) have performed constant-density simulations to reproduce the observed column densities toward HD 185418, and deduce a slightly higher number density and a substantially higher cosmic-ray ionization rate than a previous study had indicated (Sonnentrucker et al. 2003). It will be exciting to see what impact Cloudy will have as additional sightlines are modeled.

5.4. Challenges to the models

Although the models of diffuse clouds are quite advanced (compared to those used for dense clouds) in terms of their treatment of physical processes (especially radiative processes), they are still in a relatively immature state in terms of the number of chemical species and reactions considered. Furthermore, the models are hampered by our lack of a good physical understanding of clouds, and especially of processes such as turbulence and their coupling to the chemistry. Not surprisingly, there are many mysteries in diffuse cloud chemistry left unsolved by the current generation of models. The eventual solution of these mysteries will likely lead us to an improved understanding of the physical and/or chemical conditions in the diffuse ISM.

5.4.1. CH$^+$. The large observed abundance of CH$^+$ (first identified by Douglas & Herzberg 1941) has been a constant problem for steady-state equilibrium models of the chemistry. The fundamental difficulty is that the reaction C$^+$ + H$_2$ → CH$^+$ + H is endothermic by 4650 K and does not proceed at interstellar temperatures of ~100 K. The only other known formation mechanism is the radiative association reaction C$^+$ + H → CH$^+$ + hν (or C$^+$ + H$_2$ → CH$_2^+$ + hν followed by photodissociation of CH$_2^+$), which has a very small rate coefficient ~10^{-16} cm^3 s^{-1} (Graff et al. 1983). Not only is CH$^+$ expected to be produced very slowly, but it is destroyed rapidly by reaction with H, H$_2$, or electrons. Consequently, models such as van Dishoeck & Black's (1986b) underpredict the CH$^+$ abundance by about two orders of magnitude.

There seems no way out of this quandary, unless some very important formation pathway is being overlooked or unless all of the destruction pathways are slower than expected (for example, due to quantal effects at low temperatures). The most popular solution to this problem has been to invoke some sort of nonequilibrium process that provides enough energy to overcome the endothermicity of the reaction C$^+$ + H$_2$ → CH$^+$ + H.

The challenge is to identify a physical mechanism that can drive this endothermic reaction without "breaking" the rest of the chemistry. For example, a simple invocation of a shock is difficult, as it would also drive other endothermic reactions such as O + H$_2$ → OH + H, thereby overproducing OH (which is well-explained by current models) and it would lead to velocity shifts between CH$^+$ and CH (which are not observed). To avoid these problems, attention has focused on magnetohydrodynamic (MHD) effects, which offer the possibility of accelerating C$^+$ ions with less effect on the temperature of neutrals. Although much work has been done on individual MHD shocks (e.g., Draine & Katz 1986), a more recent intriguing suggestion is that the CH$^+$ production may be due to ubiquitous but intermittent dissipation of MHD turbulence (e.g., Joulain et al. 1998, Falgarone et al. 2005); this suggestion may also help account for the observed rotational excitation of H$_2$.

5.4.2. H$_3^+$. The observed large column densities of H$_3^+$ in diffuse cloud sightlines (McCall et al. 2002) pose another challenge to chemical models. The problem is that H$_3^+$ is produced following cosmic-ray ionization of H$_2$ (an infrequent occurrence), and destroyed efficiently by dissociative recombination with electrons, which are abundant in diffuse clouds. Based on simple steady-state models, the H$_3^+$ abundance should be one to two orders of magnitude lower in diffuse clouds than in dense clouds, but H$_3^+$ column densities are observed to be comparable in the two environments.

There seem to be only three possible solutions to this puzzle: (*a*) an increase in the H$_2$ ionization rate, (*b*) a decrease in the electron recombination rate coefficient, or (*c*) a decrease in the electron abundance. A low recombination rate coefficient seems to be ruled out by recent storage-ring measurements at low temperature (McCall et al. 2004, Kreckel et al. 2005) and supporting theoretical calculations (Kokoouline & Greene 2003). A decrease in electron abundance, at least in one sightline, has been ruled out by the observation of H$_3^+$ toward ζ Persei, where the electron fraction is known from UV measurements of C$^+$ and H$_2$ (McCall et al. 2003). The possibility of a low electron abundance has not been ruled out in the higher extinction sightlines

of McCall et al. (2002), but seems unlikely; a search is currently underway for H_3^+ in additional classical diffuse cloud sightlines (B. J. McCall, private communication).

The observations seem to suggest that the enhanced H_3^+ abundance is a by-product of higher ionization rates than normally assumed, either by X-ray and UV photoionization (Black 2000) or by an enhanced cosmic-ray ionization rate (McCall et al. 2002, 2003). MHD shocks have been considered, but are unable to produce H_3^+ (Le Petit, Roueff & Herbst 2004). The suggestion of a higher cosmic-ray ionization rate in diffuse clouds has recently been revived by Liszt (2003); this theory was shown to be marginally compatible with OH chemistry (Le Petit et al. 2004), and has received some theoretical support from Padoan & Scalo (2005). In attempting to reconcile their observations with gas-phase chemistry models, McCall et al. (2003) required an ionization rate some 40 times higher than the canonical value. The repercussions of this enhancement for other molecular species need to be fully analyzed, and very recent models (e.g., Le Petit, Roueff & Herbst 2004) have been only marginally consistent with the observations.

5.4.3. Other challenges. There are a host of other challenges to chemical models. One is explaining the abundance and excitation of C_3 (Ádámkovics, Blake & McCall 2003) and the observed low upper limits to the column densities of C_4 and C_5 (Maier, Walker & Bohlender 2004), which models predict to be more abundant than C_3 at large visual extinctions (Roueff et al. 2002). Models (e.g., van Dishoeck & Black 1986b) also underpredict the column densities of CO. Sufficient production of molecules observed at radio wavelengths, including HCO^+, C_2H, and C_3H_2, poses perhaps an even greater challenge. Finally, the existence of the large polyatomic molecules responsible for the unidentified infrared bands and the diffuse interstellar bands is perhaps the biggest mystery of all (see below).

6. VERY LARGE MOLECULES IN DIFFUSE CLOUDS

One of the most astonishing developments in diffuse cloud research in the past twenty years has been the realization that very large organic molecules may be highly abundant. Here we refer to molecules containing tens or hundreds of atoms, rather than the diatomics and several-atom molecules discussed above—and in fact much more massive than the largest species yet identified in dense molecular clouds.

There are two general lines of evidence for the presence of these large organics in the diffuse ISM: a series of infrared emission features known as the Unidentified Infrared Bands (UIBs); and the long-known but still unidentified diffuse interstellar bands (DIBs) seen in the visible absorption spectra of reddened stars.

6.1. Unidentified Infrared Bands (UIBs)

Gillette, Forrest & Merrill (1973) first noticed a series of unidentified infrared emission features in H II regions, and subsequent observations revealed the same bands in carbon-rich planetary nebulae and some carbon star atmospheres. The strongest UIBs occur at 3.3, 6.2, 7.7, and 11.3 μm, wavelengths indicative of vibrations in

sp^2-hybridized hydrocarbons, such as aromatic molecules. Allamandola & Norman (1978) and Allamandola, Greenberg & Norman (1979) suggested that these features might be due to vibrational emission from complex hydrocarbons (in solid state) following UV excitation. Duley & Williams (1981) suggested polycyclic aromatic hydrocarbons (PAHs) as the responsible species, but still in solid form (loosely attached to small interstellar grains). Léger & Puget (1984) suggested that free PAH molecules, i.e., in the gas phase, could be responsible for the observed emission (for a comprehensive review of the PAH hypothesis, see Allamandola, Tielens & Barker 1989).

The general mechanism invoked to explain the UIBs is absorption of a UV photon, followed by relaxation to an excited vibrational state of the ground electronic state, and subsequent emission of IR photons as the molecule transitions to the ground vibrational state. This hypothesis was developed in the work of Sellgren (1984), who showed that only very small grains or large molecules could be stochastically heated sufficiently to produce the observed IR emission following the absorption of a single UV photon. As reviewed by Geballe (1997) and Peeters et al. (2004), UIBs have been observed in a wide range of astrophysical environments where gas and dust is exposed to radiation, including planetary nebulae, H II regions, reflection nebulae, post-AGB stars, young stellar objects, and novae.

The existence of UIB carriers in diffuse molecular clouds also seems probable. There have been some detections of the UIB bands in absorption (Sellgren et al. 1995, Bregman et al. 2000, Chiar et al. 2000, Song et al. 2003), but these have been in dense cloud sightlines or toward the Galactic Center, where both dense and diffuse gas are present. Observations using ISO (Kahanpää et al. 2003) and IRTS (Sakon et al. 2004) have shown the presence of the UIBs in nondescript regions of the galactic plane, suggesting that the UIBs may be prevalent throughout the diffuse ISM. Most researchers in the field agree that the UIBs are caused by some sort of aromatic hydrocarbons, or carbonaceous material that contains aromatic groups. As discussed by Tokunaga (1997), the identification of the UIBs with gas-phase classical PAH molecules (such as coronene) is very popular but is not definitive, and other potential carriers could include very small particles of materials such as quenched carbonaceous composite (QCC), hydrogenated aromatic hydrocarbon (HAC), and coals.

Despite the uncertainties surrounding the exact nature of the carriers of the UIBs, it is clear that they represent an important component of the molecular and/or grain inventory of the ISM in general, and likely also in diffuse molecular clouds.

6.2. Diffuse Interstellar Bands (DIBs)

The first notice given to diffuse unidentified features in the spectra of distant stars came more than 80 years ago, when Heger (1922) reported, on the basis of spectra obtained in 1919, a pair of "stationary" features at 5780 and 5797 Å in spectroscopic binaries. A decade later, Merrill and others took up the pursuit of these features (e.g., Merrill 1934, 1936). The term "diffuse interstellar bands" was coined: "diffuse" because the absorption features are broader than atomic lines and resemble typical

molecular bands, and "interstellar" because by then there was general acceptance of the notion that the "stationary" lines were formed in the space between the stars.

Several prominent astronomers of the day considered it likely that the DIBs were formed by molecules in the ISM (e.g., Russell 1935, Eyster 1937, Swings 1937), but in time the emphasis swung to solid-state absorption as the origin of the DIBs (e.g., Herbig 1963, Duley 1968, Huffman 1970, and many others—see review by Snow 1995) as formation mechanisms for maintaining a sufficient population of gas-phase molecules were not known. But in the 1960s and 1970s, when the first radio-wavelength detections of molecules occurred (Weinreb et al. 1963, Rank et al. 1971) and concurrently astronomers realized that rapid molecular formation through ion-neutral reactions was possible, molecules in the diffuse ISM received new respect. The notion that the DIBs are formed by molecules regained favor, and several researchers proposed specific mechanisms for producing the observed features by molecular transitions, including some types of transitions that could occur in relatively small and simple species (e.g., Danks & Lambert 1976, Douglas 1977). Smith, Snow & York (1977) summarized arguments against a solid-state origin of the DIBs and those favoring a molecular carrier. The most powerful of arguments favoring gas-phase carriers are the observed constancy of DIB wavelengths and profiles from sightline to sightline (these should vary if solid-state transitions were responsible; see, for example, Smith, Snow & York 1977; also M. Drosback, T. Snow, J. Thorburn, S. Friedman, L. Hobbs, et al., in preparation) and the existence of fine structure in some DIBs (e.g., Sarre et al. 1995).

As suggested by Herbig (1993, 1995), the majority of the strong DIBs are most abundant in the atomic hydrogen gas and are not closely associated with dense molecular clouds or perhaps even diffuse molecular clouds. These inferences are based on the fact that the correlations of DIBs with atomic hydrogen are much stronger than correlations with H_2, and that the DIBs are weak (relative to reddening) in dense clouds (e.g., Wampler 1966; Adamson, Whittet & Duley 1991). Thus many of the DIB carriers appear to exist primarily in the diffuse atomic clouds, where hydrogen is atomic and the radiation environment is harsh. However, a subset of the DIBs (called the "C_2 DIBs"; Thorburn et al. 2003) does appear to be abundant in diffuse molecular clouds (Ádámkovics, Blake & McCall 2005). The DIB carriers are likely to be fairly large molecules and the breadth of the DIBs is likely due to unresolved rotational structure and/or intramolecular vibrational relaxation (IVR). The behavior of the DIBs with respect to incident radiation field further suggests that at least some DIB carriers may be ionized molecules (e.g., Sonnentrucker et al. 1997).

Although the exact nature of the molecules responsible for the DIBs is still not known, some clues can be gleaned from observational evidence. It is widely assumed that the DIB carriers are composed of cosmically abundant elements (such as H, C, O, and N), out of concern that molecules containing trace elements may not be abundant enough to account for the large number of DIBs (at least 200; Tuarisig et al. 2000) and their overall strength. It is also widely assumed that DIBs are "organic" in nature, because carbon has a sufficiently rich chemistry to support the wide variety of individual species probably needed to explain the DIBs (for a review of the arguments favoring large organic species as DIB carriers, see Snow 2001, and references cited therein).

The following simple order-of-magnitude argument shows that there is enough carbon available to produce the DIBs. A hypothetical line of sight with $N_H \sim 10^{22}$ cm^{-2} (roughly equivalent to the most reddened stars routinely observed for DIBs) would possess a total equivalent width of DIBs of about 22 Å. Assuming the DIB transitions are unsaturated, the column density of DIB carriers is of order $N = 10^{14}/f$, where f is the typical oscillator strength for the transitions. If each carrier molecule contains m carbon atoms, then the required carbon column density is $N_C = 10^{14}$ m$/f$. According to interstellar gas abundance studies (e.g., Snow & Witt 1995), the amount of carbon left over after accounting for the observed gas-phase carbon plus the amount of carbon needed to satisfy dust models is at most 10 ppm, or a column density of roughly 10^{17} cm^{-2} toward our hypothetical reddened star. As long as the ratio m$/f$ is less than 10^3, there should be enough carbon available. Because the f-value may approach or even exceed unity for allowed transitions in large molecules, there is plenty of carbon. This argument does not immediately rule out atoms containing less abundant elements, as long as f is large and m is small.

Much of the speculation about which specific molecules form the DIBs is centered on two classes of molecules: PAHs and carbon chains. The speculation about PAHs is motivated by the likely aromatic nature of the UIB carriers and their probable presence in diffuse clouds; in contrast, the speculation about carbon chains is motivated by the fact that many of the molecular species observed in cold dense molecular clouds are carbon chains (though carbon chains represent only a small fraction of the total molecular mass in these clouds—the apparent preponderance of carbon chains is in part a selection effect, because these species have high dipole moments and are therefore more likely to be detectable than other classes of molecules). Constraints on possible carriers in the PAH and carbon chain families have recently been discussed by Ruiterkamp et al. (2005) and Maier, Walker & Bohlender (2004), respectively. However, we should keep in mind the rich diversity of chemistry, and consider the likelihood that we have simply not yet thought of the best candidates for the DIB carriers.

Because many of the molecules proposed as possible carriers have accessible electronic transitions in the UV, useful insight into the nature of the DIB carriers may be gained by extending the study of DIBs to UV wavelengths. However, several obstacles make this difficult: the far-UV extinction rise limits studies to much lower A_V than optical observations; hot stars have intrinsically complex UV spectra; and other atomic and molecular interstellar lines create confusion, especially below 1108 Å where strong H_2 bands begin to dominate the spectra of reddened stars. Two general searches for UV DIBs have been carried out without any significant detections (Snow, York & Resnick 1977, using IUE data; Clayton et al. 2003, on the basis of high-quality HST/STIS spectra). Tripp, Cardelli & Savage (1994) reported a weak feature near 1369 Å in a HST/GHRS spectrum of ζ Oph that they suggested might be a UV DIB, but Watson (2001) later assigned this feature to a predissociative transition of the CH molecule. One of the goals of the science team for the Cosmic Origins Spectrograph is to extend the search for UV DIBs to greater extinction than has been probed so far.

Although observational studies can provide important insights into the nature of the DIB carriers, their rigorous identification will only come through laboratory

studies showing precise and specific spectral matches with the observed astronomical features. Such laboratory studies are challenging, because most DIB carrier candidates are not stable under terrestrial conditions and are difficult to produce in large quantities for spectroscopic study. Until recently, most work was done using frozen rare gas matrices (where large number densities could be accumulated), but such "matrix spectra" suffer from wavelength shifts and band broadening, which are difficult to quantify with sufficient precision to unambiguously compare with interstellar (gas-phase) absorption features. The formidable task of measuring gas-phase spectra of carbon chains and PAH ions has been undertaken by a few groups in the past decade, with some success (Tulej et al. 1998, Ruiterkamp et al. 2002, Biennier et al. 2003), but as yet these efforts have yielded no specific identifications of DIB carriers. There have been some near matches (such as in the case of C_7^-; Tulej et al. 1998), but these have not stood up to the standards of high-resolution spectroscopy once higher quality laboratory (Lakin et al. 2000) and astronomical (McCall et al. 2001) spectra became available. In addition to these spectroscopic studies, the chemical viability of various DIB carrier candidates has been tested through laboratory measurements of reaction rates with the most common neutral reaction partners expected in the diffuse ISM, such as atomic and molecular hydrogen, atomic oxygen, and atomic nitrogen (Snow et al. 1995; Le Page et al. 1999a,b; Barckholtz, Snow & Bierbaum 2001).

The problem of the DIBs, which has been called the longest standing mystery in all of spectroscopy, has received much more attention within the past decade or so than previously, when these unidentified features were widely considered to be curiosities but not necessarily significant. The enhanced focus on the DIBs has come about owing to the availability of very high-quality spectra that allow very precise measurements of wavelengths and profiles, the growing recognition that the DIB carriers may represent an enormous reservoir of complex organics in the diffuse ISM, and the involvement of chemists as well as astronomers in the pursuit. In contrast to the UIBs, which are very broad and represent vibrational transitions that generally indicate only the type of chemical bond involved, the DIBs are relatively narrow and represent electronic transitions that tend to be unique for every molecule. These properties of the DIBs provide hope that the coming decades may finally yield the identification of at least some of the DIB carriers. The ultimate identification of the DIB carriers will likely more than double the known inventory of interstellar molecules, and will open a whole new window into the chemistry of diffuse clouds. Additionally, once the DIB carriers are known and their chemistry understood, the DIBs may represent a powerful multidimensional probe of the physical conditions (temperature, density, radiation field, etc.) in diffuse clouds.

6.3. The Formation of Large Molecules in Diffuse Clouds

Gas-phase chemistry models for diffuse clouds (e.g., van Dishoeck & Black 1986b, Le Petit et al. 2004) normally do not address the formation of large species such as PAHs or carbon chains—though some work on modeling their effects on the chemistry and heating of clouds has been done (Lepp & Dalgarno 1988, Lepp et al. 1988).

One possibility is that these large organic species form in the gas phase in dense molecular clouds, and are then cycled back into the diffuse ISM (e.g., Bettens & Herbst 1996). But it is not clear that sufficient quantities of these species to account for the UIBs and the DIBs can be produced in this way. Another possibility is that the large organics are formed in the outflows from carbon-rich giant stars late in their evolution (Frenklach & Feigelson 1989; Latter 1991; Cherchneff, Barker & Tielens 1992; Giard et al. 1994). Under highly constrained conditions (density, velocity law of the outflow, and initial temperature) it may be possible to form the observed quantities in this way, and it is widely accepted that carbon star atmospheres may be a major source of large organics in the general ISM. Yet another closely related possibility is that large molecules in the diffuse ISM are the result of shock-induced destruction of graphitic or carbonaceous grains, some of which may have initially formed in carbon star outflows. For example, graphite essentially consists of stacked layers of fused carbon rings with very weak bonding between layers. When such a grain is shattered in a shock, the fragments will be planar fused carbon ring species, which, if they acquire peripheral hydrogen atoms, would become PAHs.

Any discussion of the origin of the large organics in diffuse clouds is necessarily speculative at this point. But apparently these species are present, and it is of great interest to understand how they came to be.

7. SPECIFIC CLOUDS OF SPECIAL INTEREST

Having reviewed the general properties and the models of diffuse clouds, here we turn our attention to a small number of specific sightlines that are often cited, either as "typical" diffuse clouds, or as possibly dominated by diffuse molecular clouds.

7.1. Prototypical Examples of Molecule-Bearing Diffuse Clouds

Many of the studies of diffuse cloud molecules cited in this review have been based on a small number of widely-studied "typical" sightlines toward certain hot stars. These stars get most of the attention not necessarily because their sightlines are typical, but because of their bright apparent magnitudes, their intrinsically clean spectra, and the evidence for their having significant molecular column densities. Hence these cases are in fact highly selected with a bias toward high molecular abundances.

7.1.1. ζ Ophiuchi (HD 149757; O9Ve, V = 2.58, Av = 1.06). By far the most frequently cited diffuse cloud sightline is that toward ζ Ophiuchi. The total hydrogen column density is 1.4×10^{21} cm^{-2}, with some 56% of the nuclei in molecular form (Morton 1975). Most of the species cited in **Table 2** have been observed in this line of sight, many of them first detections. Given this history, ζ Oph has been a target of intense scrutiny in several surveys of interstellar lines, including the very high-S/N visible-wavelength study of Shulman, Bortolot & Thaddeus (1974), in which several new species were detected; and the classic *Copernicus*-based survey of UV spectral lines carried out by Morton (1974, 1975), which remains a standard in the field.

Table 2   Molecules detected in diffuse molecular clouds

Weight	Species	Method	Target	$N(X)/N_H$	Reference
2	H_2	UV	ζ Oph	0.56	1
3	HD	UV	ζ Oph	4.5 (-7)	2
3	H_3^+	IR	ζ Per	5.1 (-8)	3
13	CH	Optical	ζ Oph	1.5 (-9)	4
13	CH^+	Optical	ζ Oph	2.4 (-8)	5
14	$^{13}CH^+$	Optical	ζ Oph	3.5 (-10)	6
15	NH	Optical	ζ Oph	6.2 (-10)	7
17	OH	UV	ζ Oph	3.3 (-8)	8
24	C_2	Optical	ζ Oph	1.3 (-8)	9
25	C_2H	mm abs.	BL Lac	1.8 (-8)	10
26	CN	Optical	ζ Oph	1.9 (-9)	11
27	HCN	mm abs.	BL Lac	2.6 (-9)	12
27	HNC	mm abs.	BL Lac	4.4 (-10)	12
28	N_2	UV	HD 124314	3.1 (-8)	13
28	CO	UV	X Per	6.4 (-6)	14
29	HCO^+	mm abs.	BL Lac	1.5 (-9)	15
29	HOC^+	mm abs.	BL Lac	2.2 (-11)	15
29	^{13}CO	UV	X Per	8.9 (-8)	16
29	$C^{17}O$	UV	X Per	7.4 (-10):	16
30	$C^{18}O$	UV	X Per	2.1 (-9):	16
30	H_2CO	mm abs.	BL Lac	3.7 (-9)	17
36	C_3	Optical	ζ Oph	1.1 (-9)	18
36	HCl	UV	ζ Oph	1.9 (-10)	19
38	C_3H_2	mm abs.	BL Lac	6.4 (-10)	10
44	CS	mm abs.	BL Lac	1.6 (-9)	20
64	SO_2	mm abs.	BL Lac	≤ 8.2 (-10)	20

Note: To facilitate comparisons we include, where possible, data on different molecules for the same source. One exception is CO, where there are ζ Oph data but we chose to list X Per instead, to allow a comparison among all the observed isotopomers. For millimeter-wave studies we have listed only BL Lac because an estimated $N_H \sim 1.7 \times 10^{21}$ cm^{-2} was available. Liszt & Lucas have detected, in other lines of sight, the additional species SO, SiO, H_2S, and HCS^+. Other values of N_H are 1.4×10^{21} cm^{-2} (ζ Oph), 1.6×10^{21} cm^{-2} (ζ Per), 3.1×10^{21} cm^{-2} (HD 124314), and 2.2×10^{21} cm^{-2} (X Per).

References: (1) Savage et al. 1997; (2) Lacour et al. 2005; (3) McCall et al. 2003; (4) Danks et al. 1984; (5) Lambert & Danks 1986; (6) Stahl & Wilson 1992; (7) Crawford & Williams 1997; (8) Roueff 1996; (9) Lambert et al. 1995; (10) Lucas & Liszt 2000b; (11) Federman et al. 1984; (12) Liszt & Lucas 2001; (13) Knauth et al. 2004; (14) Sheffer et al. 2002a; (15) Liszt et al. 2004; (16) Sheffer et al. 2002b; (17) Liszt & Lucas 1995; (18) Oka et al. 2003; (19) Federman et al. 1995; (20) Lucas & Liszt 2002.

This sightline has also been the subject of many chemical modeling efforts. For example Black & Dalgarno (1977) developed the first comprehensive diffuse cloud model taking into account not only an extensive network of chemical reactions but also physical processes and the effects of dust extinction. Their best fit to the line of sight consisted of two clouds (whose existence and velocity separation were inferred

from Doppler structure in the observed absorption lines): one low temperature, high-density cloud containing most of the mass and nearly all of the molecules; and a secondary cloud of higher temperature and lower density, blue-shifted with respect to the main component, that is more highly ionized and produces the high-J lines of H_2. Later, more comprehensive models of diffuse cloud chemistry often used the ζ Oph sightline for comparison (e.g., van Dishoeck & Black 1986b; see also comments in Heck et al. 1993).

7.1.2. X Persei (HD 24534; O9Ve, V = 6.13, Av = 2.05).

As an X-ray source (attributed to a neutron star companion), X Per is the only early-type star bright enough in both UV and X-ray wavelengths to allow high-S/N observations of both the gas absorption lines and the gas-plus-dust X-ray absorption edges, thus allowing a complete analysis of the depletions, the dust content, and the chemical and physical state of the gas in the same line of sight. Recently Cunningham, McCray & Snow (2004) have taken advantage of this to evaluate the distribution of oxygen between gas and dust, yielding useful constraints on dust models.

Earlier, the sightline toward X Per had been recognized as having a very rich molecular content (Lien 1983, 1984), with strong optical CH and CN lines as well as CO emission observed at millimeter-wavelengths and UV absorption bands of CO observed with the IUE. More recently, UV CO bands have been observed with the HST/GHRS and analyzed by Kaczmarczyk (2000a,b), who used a statistical fitting method to several bands to derive a column density of roughly 10^{-5} times the total hydrogen abundance in the line of sight. More recently Sheffer et al. (2002b) found similar results based on STIS spectra of intersystem CO lines. Though X Per is fainter than ζ Oph, it shows more promise as a standard for observing and interpreting diffuse molecular clouds, particularly because of its unique status as an X-ray source.

7.1.3. Other sightlines.

Other widely-studied "typical" diffuse cloud sightlines that have been the focus of various molecular studies include ζ Persei and o Persei (Chaffee 1974; Snow 1975, 1976b, 1977; Snow, Lamers & Joseph 1987; Crutcher & Watson 1976a,b; McCall et al. 2003); and several of the bright OB stars in the ρ Ophiuchi cloud (Carrasco, Strom & Strom 1973; Snow & Cohen 1974; Snow & Jenkins 1980; Snow 1983) where the UV dust extinction is low and the molecular fraction small.

7.2. Three Sightlines Dominated by Diffuse Molecular Clouds

Most sightlines are best interpreted as due to a mixture of diffuse atomic and diffuse molecular clouds, but there are a few cases where the diffuse atomic material seems to be relatively insignificant or even absent, thus revealing the properties of diffuse molecular clouds alone. Here we describe three such cases, each of which is characterized by an extremely steep far-UV extinction rise, exceptionally high molecular abundances, and relatively weak strengths of the most common diffuse interstellar bands (which are mostly associated with diffuse atomic gas). A fourth case, that toward HD 29647 behind the Taurus dark cloud (Snow & Seab 1980, Crutcher 1985), is

confounded by extreme observational difficulties because of a profusion of photo-spheric lines in the visible spectrum.

7.2.1. HD 62542 (B5V; V = 8.04; Av = 1.1). This star lies behind a portion of the Gum nebula, and was found to have a UV extinction curve very similar to that of HD 29647, with a very broad and weak 2175 Å bump and a steep far-UV rise (Cardelli & Savage 1988), which may be attributed to mantle growth over small carbonaceous grains, suppressing the extinction bump (Mathis & Cardelli 1992, Mathis 1994). The infrared extinction curve is very close to the galactic average, in strong contrast to the unusual UV curve (Whittet et al. 1993), suggesting that no significant grain growth has occurred. Visible-wavelength spectroscopic studies by Cardelli et al. (1990) and by Gredel, van Dishoeck & Black (1993) showed that the molecular abundances are very high for the amount of extinction, and that the density is high enough to cause excess excitation of CN above the radiation temperature of the cosmic microwave background. Detailed modeling of the CN rotational excitation (Black & van Dishoeck 1991) yielded a gas kinetic temperature of 50 K and a cloud density in the range from 500 to 1000 cm^{-3}. There is enough UV flux for FUSE observations, resulting in a direct measurement of $N(H_2)$ (Rachford et al. 2002), but N(H) cannot be measured owing to the late spectral type of the star (at spectral type B5 and later, stellar Lyman-α absorption totally obscures the interstellar line), so f_{H_2} is unknown. Ádámkovics, Blake & McCall (2005) have used optical surrogates to estimate $f^N_{H_2} \sim$ 0.8. High-resolution optical spectra show that the line of sight is dominated by a single component (D. Welty, private communication).

As discussed by Snow et al. (2002), the DIBs in this sightline are extremely weak. Ádámkovics, Blake & McCall (2005) have pressed the issue with higher-resolution and S/N spectra, and now have reported the clear detection of several DIBs, most of them among the so-called "C_2 DIBs." They conclude that the line of sight toward HD 62542 is dominated by a single diffuse molecular cloud core, without any accompanying outer diffuse atomic cloud. This is consistent with the speculation by Cardelli et al. (1990) that the diffuse outer portions of the cloud could have been evaporated by the intense UV radiation of the nearby O stars ζ Puppis and γ^2 Velorum.

7.2.2. HD 204827 (B0V; V = 7.94; Av = 3.0). This sightline was identified by Cardelli, Clayton & Mathis (1989) as having anomalously steep far-UV extinction, and recent measurements have revealed very high molecular abundances. This line of sight is distinguished by having by far the strongest C_3 absorption yet observed (Oka et al. 2003). The breadth of the C_3 lines suggests the possibility that there are at least two strong molecular components—in addition, Pan et al. (2004) found several velocity components in CN toward this star. Unfortunately, because of its relatively faint apparent magnitude and especially because of its very steep UV extinction rise, HD 204827 is far too dim in the UV for HST or FUSE observations. As a consequence we have no direct information on its hydrogen column density or molecular fraction. Using molecular and DIB proxies, Ádámkovics, Blake & McCall (2005) have estimated a H_2 molecular fraction of about 0.6, and suggest that this sightline consists

Table 3   Molecules not detected in diffuse molecular clouds

Weight	Species	Method	Target	$N(X)/N_H$	Reference
14	CH_2	UV	ζ Oph	≤2.4 (−8)	1
15	NH^+	UV	ζ Oph	<8.7 (−10) f^{-1}	2
18	H_2O	UV	HD 154368	<2 (−9)	3
24	NaH	UV	ζ Oph	<1.2 (−9)	2
25	MgH	UV	ζ Oph	<3.0 (−8)	2
25	MgH^+	UV	ξ Per	<1.0 (−10) f^{-1}	2
26	CN^+	UV	ξ Per	<5.3 (−10)	2
28	CO^+	UV	ζ Oph	<4.1 (−9)	2
28	AlH	UV	ζ Oph	<1.3 (−10) f^{-1}	2
29	SiH	UV	ζ Oph	<1.0 (−9)	2
29	N_2H^+	mm abs.	various	—[b]	4
30	NO	UV	ξ Per	<1.2 (−6)	2
30	NO^+	UV	ζ Oph	<5.9 (−8)	5
32	O_2	UV	o Per	<1.8 (−10) f^{-1}	2
33	SH	UV	o Per	<7.6 (−11) f^{-1}	2
37	C_3H	mm abs.	various	—[b]	6
41	CaH	UV	ζ Oph	<4.9 (−11) f^{-1}	2
41	CH_3CN	mm abs.	various	—[b]	4
44	CO_2	UV	ζ Oph	<1.5 (−9) f^{-1}	2
44	SiO	UV	ζ Oph	<1.7 (−10) f^{-1}	2
48	C_4	Optical	ζ Oph	<2.6 (−10)	7
49	C_4H	mm abs.	various	—[b]	6
50	HC_4H^+	Optical	HD 207198	<1.4 (−9)	8
52	$C_4H_4^+$	Optical	—[a]	<2 (−10)	9
60	C_5	Optical	ζ Oph	<5.3 (−11)	7
61	C_5H	Optical	—[a]	<1 (−10)	10
73	C_6H	Optical	HD 207198	<3 (−10)	8
74	HC_6H^+	Optical	HD 210839	<1.3 (−10)	8
75	HC_5N^+	Optical	HD 207198	<1.7 (−10)	8
76	$C_6H_4^+$	Optical	—[a]	<5 (−11)	11
76	NC_4N^+	Optical	HD 210839	<1 (−10)	8
85	C_7H	Optical	—[a]	<1 (−10)	10
86	HC_7H	Optical	—[a]	<1 (−9)	12
97	C_8H	Optical	HD 207198	<3 (−10)	8
98	HC_8H^+	Optical	HD 207198	<3 (−10)	8
100	$C_8H_4^+$	Optical	—[a]	<6 (−11)	9
109	C_9H	Optical	—[a]	<1 (−10)	10
110	HC_9H	Optical	—[a]	<1 (−9)	12
121	$C_{10}H$	Optical	HD 207198	<5 (−10)	8
134	$HC_{11}H$	Optical	—[a]	<5 (−9)	12

(*Continued*)

Table 3 (*Continued*)

Weight	Species	Method	Target	N(X)/N$_H$	Reference
145	C$_{12}$H	Optical	HD 207198	<5 (−10)	8
158	HC$_{13}$H	Optical	—[a]	<5 (−9)	12
720	C$_{60}$	Optical	Cyg OB2 8A	<4.8 (−11)	13

[a]Limit is not from a dedicated search, but from absence of known DIB coincident with laboratory wavelength; N$_H$ is assumed to be 10^{22} cm^{-2}.

[b]No value of N$_H$ is available for these extragalactic sightlines.

References: (1) Lyu et al. 2001; (2) Tabulated in Snow 1979; (3) Spaans et al. 1998; (4) Liszt & Lucas 2001; (5) Federman et al. 1995; (6) Lucas & Liszt 2000b; (7) Maier et al. 2004; (8) Motylewski et al. 2000; (9) Araki et al. 2004; (10) Ding et al. 2002; (11) Araki et al. 2005; (12) Ding et al. 2003; (13) Herbig 2000.

of both a diffuse cloud core (diffuse molecular cloud) and an envelope (diffuse atomic cloud material).

7.2.3. HD 210121 (B3V; V = 7.67; A$_V$ = 1.2). This star lies at high galactic latitude and appears to lie behind the core of a molecular cloud (Désert, Bazell & Boulanger 1988; de Vries & van Dishoeck 1988). Gredel et al. (1992) published a comprehensive analysis of this sightline, including millimeter-wave emission observations and optical absorption line data. Welty & Fowler (1992) carried out another broad study of this line of sight, incorporating high-resolution optical spectra with UV measurements of the extinction curve and of interstellar gas absorption lines (obtained with the IUE). Based on these two analyses, the radiation field impinging on the cloud appears to be less intense than in most sightlines, and the material along the sightline appears to be clumpy in nature. Based on an analysis of C$_3$ absorption, Roueff et al. (2002) inferred that the characteristic density is several times higher than that in more classical diffuse clouds. Larson, Whittet & Hough (1996) examined the extinction and polarization properties of the dust, and concluded that small grains dominated and little grain growth has occurred.

It appears that the line of sight toward HD 210121 is a very good case where a single cloud complex can be studied without interference from foreground material, because of the high galactic latitude of the star and the evidence of a rich chemistry not dominated by radiation.

8. CONCLUDING REMARKS

The past three decades have seen enormous advances in our understanding of the physical and chemical complexity of diffuse interstellar clouds. In this review we have attempted to summarize recent work on diffuse clouds containing a molecular component, which we call diffuse molecular clouds under the nomenclature that we are proposing for categorizing interstellar clouds.

We have summarized the known interstellar molecules in diffuse molecular clouds and have described how the observations can be used to derive information on cloud physical conditions such as density and radiation field intensity. We have found that

much of the chemistry of diffuse molecular clouds can be well represented by existing models—though no models that take into account all of the processes known to be important are yet available.

Several outstanding mysteries remain: The origins of some simple species (e.g., CH^+ and HCO^+) are not understood; the high abundance of H_3^+ in diffuse molecular gas is a mystery; the possible role of grain surface reactions in the formation of molecules other than H_2 is as-yet not defined; and perhaps most puzzling are the origin and role of large organic species whose presence is inferred from observations of IR emission features and the optical diffuse interstellar bands (we do not even know whether the same family of molecules is responsible for both phenomena).

We can suggest several areas for future research, some realistic in the near term and others that will take time. First and foremost, existing telescopes and spectrographs can significantly improve the optical and IR spectra of reddened stars to the point where species expected to be abundant will either be detected or their absence will conflict with existing models. The list of species in **Table 3**, which consists of upper limits only, provides a starting point.

Another potentially fruitful area for future work might be to obtain high-sensitivity IR absorption spectra of reddened stars behind diffuse molecular clouds, to achieve overlap between optical (and possibly UV) absorption line measurements and IR absorption lines in the same lines of sight. A wealth of new physical data will become available if this can be done. Like most ISM absorption-line projects on reddened stars, this will require substantial amounts of observing time.

We advocate further intensive searches for millimeter-wave absorption due to polyatomic species, along the line of the Liszt & Lucas surveys, toward additional sources for which optical and UV (and in principle, IR) absorption-line spectra exist or can be obtained.

Finally, we emphasize the need for more sensitive UV spectroscopic instruments to probe denser clouds through absorption line techniques. When/if the Cosmic Origins Spectrograph is installed aboard the HST, it may become feasible to perform sensitive searches for the UV electronic transitions of PAHs and other large organic species.

ACKNOWLEDGMENTS

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Contents

Indexes

Errata

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