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Interstellar Molecules *

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Summary. The study of interstellar molecules broadly includes two areas of interest. One area uses the unique ability of molecules to act as probes of the physical conditions in the cold, dense, visually opaque component of the interstellar medium. The physical properties of this and other components of the interstellar medium are summarized. The other area deals with the chemistry of interstellar molecules, recent aspects of which are emphasized in this review. Gas-phase chemistry, shock chemistry, and grain surface chemistry are discussed in the context of recent observations. No present observations suggest that surface reactions are relevant, but neither can they be ruled out. Ion-molecule reactions are clearly operative, at least for the simpler species. Chemical isotope fractionation is reviewed, andd it is concluded that the complexities of the chemistry allow no cosmological conclusions to be drawn from observations of deuterium in interstellar molecules, while the presence of ^{13}C in interstellar molecules permits an estimate of the $^{12}C/^{13}C$ ratio which is consistent with the current concepts of the nucleosynthesis history of the Galaxy. Possible connections between interstellar molecules and the early molecular history of the solar system are discussed.

Key words: Molecules – Interstellar – Chemistry – Isotopes – Solar system

I. Introduction

Interstellar molecules have been a major field of astrophysical investigation for about 10 years. As of June, 1979, 53 species are known, and the discovery rate is about 4 per year. The known species are listed in Table 1 along with the types of region in which they are found. Important areas of study are the distributions and abundances

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Table 1. Known Interstellar Molecules (June 1979)

No. of atoms	Molecule	Opt/	UV/	IR	Radio spectrum	Type of objects[a]			
2 H_2	hydrogen		x	x	---	1	2	3?	4
OH	hydroxyl radical		x		A-doubling	1	2	3	4
CH^+	methylidyne ion	x			---	1			
CH	methylidyne	x			A-doubling	1	2		
CO	carbon monoxide		x	x	rotational	1	2	3	4
CN	cyanogen radical	x			rotational	1	2	3	
CS	carbon monosulfide				rotational	1	2	3	
NO	nitric oxide				rotational		2		
C_2				x	---			3	
SO	sulfur monoxide				rotational		2		
NS	nitrogen sulfide				rotational		2		
SiO	silicon monoxide				rotational		2	3	
SiS	silicon monosulfide				rotational		2	3	
3 HCO^+	formyl ion				rotational	1	2		4
N_2H^+	---				rotational	1	2		
H_2O	water				rotational		2	3	4
HCN	hydrogen cyanide				rotational	1	2	3	4
HNC	hydrogen isocyanide				rotational	1	2	3	
CCH	ethynyl radical				rotational	1	2	3	
HCO	formyl radical				rotational		2		
HNO	nitrosyl radical				rotational		2		
OCS	carbonyl sulfide				rotational		2	3	
H_2S	hydrogen sulfide				rotational		2		
SO_2	sulfur dioxide				rotational		2		
4 NH_3	ammonia			x	inversion	1	2	3	4
H_2CO	formaldehyde				rotational, K-doubling	1	2		4
$HCCH$	acetylene			x	---			3	
C_3N	cyanoethynyl radical				rotational			3	
$HNCO$	isocyanic acid				rotational		2		
H_2CS	thioformaldehyde				rotational, K-doubling		2		
$HCNS$	isothiocyanic acid				rotational		2		
5 CH_4	methane				rotational		2		
C_4H	butadiynyl radical				rotational			3	
HC_3N	cyanoacetylene				rotational	1	2	3	
H_2CCO	ketene				rotational		2		
NH_2CN	cyanamide				rotational		2		
CH_2NH	methanimine				K-doubling		2		
$HCOOH$	formic acid				rotational, K-doubling		2		
6 CH_3CN	methyl cyanide				rotational		2		
NH_2CHO	formamide				rotational, K-doubling		2		
CH_3OH	methanol				rotational, K-doubling		2		
CH_3SH	methyl mercaptan				rotational		2		
7 CH_3CCH	methyl acetylene				rotational	1	2		
CH_3CHO	acetaldehyde				rotational, K-doubling		2		
NH_2CH_3	methylamine				rotational		2		
CH_2CHCN	vinyl cyanide				K-doubling		2		
HC_5N	cyanobutadiyne				rotational	1	2	3	

Table 1. (cont.)

8	$HCOOCH_3$	methyl formate	rotational		2		
9	CH_3CH_2OH	ethanol	rotational		2		
	CH_3CH_2CN	ethyl cyanide	rotational		2		
	CH_3OCH_3	dimethyl ether	rotational		2		
	HC_7N	cyanohexatriyne	rotational	1		3	
10	none						
11	HC_9N	cyano-octatetrayne	rotational	1			

[a] 1: dark (cold) and/or diffuse clouds; 2: HII region (warm) clouds and/or galactic center; 3: circumstellar envelopes; 4: external galaxies

of molecules in external galaxies, the morphology of galactic molecular clouds and their evolution and relation to star formation, interstellar chemistry, and the distribution of isotopes throughout the galaxy and their implications for cosmology and the nucleosynthesis history of the galaxy.

Topics concerned with the morphology of galactic molecular clouds, their evolution, their interaction with the stellar population of the galactic disk, and their relation to star formation were recently reviewed by Turner (1979). The molecular component of external galaxies is discussed by Rickard (1979). In this review, we emphasize recent developments in interstellar chemistry and in the interpretation of isotope ratios, which depends upon models of the chemistry. For this purpose, a brief summary of the physical conditions characterizing the several morphological regimes of the interstellar medium is useful.

Morphology of the Interstellar Medium[1]. Current observations suggest that the interstellar medium is comprised of several different physical regimes (Myers, 1978; Turner, 1979): (1) *'Coronal' gas* is a very hot (10^5-10^6 K), tenuous ($\sim 10^{-2}$ cm^{-3}) component revealed by absorption lines of highly ionized atoms observed in the UV; it possibly accounts for 20 to 50% of the interstellar medium by volume. (2) *Intercloud gas* is slightly cooler (10^3-10^4 K) and denser (0.1-1 cm^{-3}) and may be in pressure equilibrium with the coronal gas, in which case it would occupy roughly 30% by volume of interstellar space. (3) *Diffuse interstellar clouds* range from densitites of ~ 0.02 cm^{-3} where hydrogen (and other elements) are atomic in form and the visual extinction is $\lesssim 0\overset{m}{.}1$, to densities of $\sim 10^2$ cm^{-3}, where hydrogen is molecular, and extinctions reach $\sim 2^m$. Temperatures are of order 100 K over the entire density range, and cloud masses of a few hundred solar masses are typical. Although molecules (H_2,CO) make their first appearance in these clouds, the cloud constitution is more atomic than molecular.

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[1] Astrophysical nomenclature used here is as follows. Densities are given as particles per cm^{-3}; where the gas is molecular, a particle is an H_2 molecule since hydrogen is 10^4 times more abundant than any other molecule. Distances are in parsecs (pc) or astronomical units (AU); 1 pc = 3.26 light years; 1 AU = 1.5×10^{13} cm. Opacities (extinctions) are measured in magnitudes (m); the attenuation factor is defined as $10^{0.4\ m}$, or 5 magnitudes is a factor of 100. 1 solar mass = 2×10^{33} gm

(4) *Molecular clouds* represent the dense, cool component of the interstellar medium and, although filling only ~2% of it by volume, they account overall for at least 50% of its mass and play a dominant role in the dynamics and kinematics of the interstellar medium. In these clouds, hydrogen is essentially all molecular in form, the onset occurring sharply at an extinction of $\sim 2^m$. We may roughly divide the molecular component into *cool dark clouds* and *warm clouds*, the latter being associated with HII regions.[2] Cool, dark clouds are typically a few hundred solar masses, ~1 pc in size, and have densities in the range 10^3-10^4 cm^{-3}. They are not associated with formation of massive early-type stars and thus have no significant internal source of heat. Being opaque to UV radiation, they are apparently heated by cosmic rays and cooled by rotational excitation of CO, a balance which endows them with a narrow range of temperatures, 5-15 K. Warm molecular clouds associated with HII regions are by comparison much more massive (10^4-10^7 solar masses), much larger (~3-100 pc in extent) and much denser (having 'core' regions of 10^4-10^7 cm^{-3} or greater). The warm core(s) of these clouds are often quite localized near regions of star formation; either embedded protostellar objects or expanding HII regions created by newly formed massive stars within or at the edges of these clouds heats the surrounding dust grains and gas to temperatures as high as 70 K over quite large regions, and presumably much higher over small regions which cannot be resolved by current observational techniques. The regions far from the heated cores of these warm clouds have properties more like the cold dark clouds.

Interstellar Molecular Chemistry: General Guidelines. The chemistry of these molecular regions appears to be very complex; the formation and destruction of molecules can involve atoms, ions, free radicals, molecular ions, neutral molecules, solid surfaces, cosmic rays, energy from shocks, and radiation fields. In principle, molecules may be formed in situ within the dark, opaque clouds where they are presently seen, either in the gas phase, or on surfaces of grains that produce the extinction. Or, they may form in atmospheres of cool stars or in presolar nebulae embedded within these clouds, and be injected into the clouds. They could even be formed in and ejected from evolved cool stars known to lose mass to the interstellar medium, and subsequently make their way into dark clouds.

Fortunately, a few observed properties of interstellar molecules allow us to narrow these choices. (a) The lifetimes of typical interstellar molecules (CO, OCS, H_2CO, H_2O) are only about 100 years against photodissociation by the UV field in unshielded regions of space. Thus molecules cannot travel across open regions of space, and therefore must form within the dark clouds, or circumstellar shells where they are now seen. (b) While isotope ratios in interstellar molecules are not usually precisely terrestrial, they contrast sharply with the highly non-terrestrial ratios that characterize evolved stars known to lose mass. Again, therefore, one concludes that molecules seen in dense molecular clouds cannot have originated in the atmospheres of evolved stars. Molecules observed in circumstellar shells around evolved stars do reflect the stellar isotope ratios. (c) The considerable abundance of the ions HCO^+ and N_2H^+ shows

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[2] HII regions are regions of ionized atomic hydrogen surrounding, or adjacent to, hot young stars and ionized by their UV radiation

that ion-molecular gas-phase reactions must play an important, possibly dominant part in interstellar chemistry. (d) Laboratory and theoretical work indicate that interstellar grains must be important in the history of at least some molecules, and certainly the refractory elements, since the grains readily adsorb many species under interstellar conditions. Experimental evidence that molecules can be *formed* on grain surfaces and released into the gas phase is much less conclusive. Only H_2, among interstellar species, seems necessarily to be formed on grain surfaces.

There are other, less conclusive clues to the nature of interstellar chemistry. Some examples are as follows: (1) Carbon chemistry seems clearly favored, although an earlier belief that multiple carbon bonds predominate over saturated or single carbon bonds is no longer tenable. (2) Cyanides appear more numerous than aldehydes or alcohols, but do not appear in greater concentrations. (3) Very likely, the N-O bond is underrepresented in interstellar space, despite intense efforts to detect species in addition to the three (NO, NS, HNO(?)) already known. (4) No carbon-ring molecules are yet seen, although rather complex carbon-chain species are known. The small number of molecular ions, and even free radicals, is due to relatively few of these species having measured microwave spectra. In fact, the two molecular ions (HCO^+, N_2H^+) were identified in interstellar space before they were synthesized in the laboratory, by means of ab initio calculations of their structure, isotopic substitution, and hyperfine structure. (5) Abundances of molecules are not well related to the relative abundances of their constituent atoms. For example, Mg, S, Si are comparably abundant in atomic form, yet Mg-molecules are not seen while species containing S and Si are readily observed. Also, when compared with their oxygen counterparts, sulfur-bearing molecules have abundances often diminished by far more than the atomic abundance ratio S/O ($\approx 1/35$).

Currently suggested mechanisms of interstellar molecule formation include: (a) gas-phase, 2-body reactions at low temperatures (< 100 K); (b) gas-phase 2-body reactions at high temperatures (as occur in shocks); (c) surface chemistry on dust grains.

II. Ion-Molecule Chemistry

At the low temperatures and densities of interstellar space, gas phase reactions are restricted to those that involve only bi-molecular collisions, and negligible activation energies. Those with reasonable rates include ion-molecular reactions (including electron-recombination reactions) and a few neutral-neutral reactions that involve reasonably abundant species. Model ion-molecular chemistries, driven by cosmic-ray ionization of H_2 in cold, weakly ionized H_2 clouds, were first proposed by Herbst and Klemperer (1973) and Watson (1974). Those models predicted sizable abundances of HCO^+ and N_2H^+ before these species were identified, and also large abundances for many other known molecules; subsequent studies by many have tied the predicted astrochemical properties of these ions in satisfactorily with their observed properties.

A somewhat optimistic assessment of ion-molecule chemistry is that it has reasonably accounted for most of the known species that contain 5 or less atoms. Detailed analyses of species such as OH (Turner and Heiles, 1974; Myers, 1975), HCN (Turner and Thaddeus, 1977; Huntress and Anicich, 1976; Huntress, 1977), HNC (Herbst, 1978), NH_3 (Huntress, 1977), H_2O (Huntress and Anicich, 1976; Huntress, 1977; Herbst, 1978), and CN (Turner and Gammon, 1975) indicate reasonable quantitative agreement between observations and theory, even though only a few reactions, which seem to dominate, are included. In particular, the predicted dependence of molecular abundances upon overall particle density, as well as the abundance ratios of these fundamental species, seem borne out by the observations. More recently, complex reaction-network calculations involving hundreds of reactions and many dozens of species have been carried out (Mitchell et al., 1978; Iglesias, 1977; Prasad and Huntress, 1980). These calculations include species with at most 5 atoms, and ignore the contribution of surface chemistry on grains, although some models include adsorption onto grains in a formal sense. In general, these calculations suggest that the observed abundances of about two dozen molecular species are quite adequately described over a range of cloud densities. Included are sulfur and silicon species, and the observed under-representation of sulfur compared with oxygen in interstellar species is generally predicted. Searches in the UV for several molecules not accessible at radio wavelengths have been made with the Copernicus satellite (Jura and York, 1978; Kirby and Dalgarno, 1978; Smith and Snow, 1979). The results of these searches are also consistent with ion-molecule schemes, although in several cases the predictions are highly model-dependent upon such factors as the effect of grains on dissociating UV radiation.

Several cautionary factors should be considered in assessing these otherwise encouraging results. (a) The rates of many, if not the majority, of reactions are poorly known, and are estimated by analogy with other 'similar' reactions. (b) The results are sensitive, in general significantly so, to the input atomic abundances. Calculations have used solar abundances and various 'depletion' abundances deduced from Copernicus UV observations of *diffuse* clouds (Morton, 1974; Snow, 1976). Not only abundances of molecular species, but also the ionization structure of the cloud, depend critically upon the metal content; this is unobservable in dense clouds and is poorly known, because it depends strongly on temperature and on the nature of the grains upon which metals freeze, properties which cannot be assumed to resemble very closely the conditions found in the few (possibly unusual) diffuse clouds examined by the Copernicus satellite. (c) Some calculations (Iglesias, 1977) have included the time-dependent aspect of interstellar chemistry. An exact treatment is of course not presently possible, as the chemistry would have to be tied self-consistently to the detailed physical evolution of the cloud (cf. Glassgold and Langer, 1976) about which little is known. The time-dependent calculations to date understandably ignore these larger evolutionary questions and simply follow the chemistry forward from a switch-on time. Nonetheless they show a wide range of equilibrium times for different species, and for different cloud densities and temperatures. Prior to equilibrium, the relative abundances of most species depend strongly upon time. In clouds of density 10^3 cm^{-3} equilibrium is achieved in about 10^6 years, and an x-fold increase in the density means roughly an x-fold increase in the equilibrium time.

Because of the above considerations, it is not surprising that closer examination of certain species has revealed less satisfactory agreement between observation and theory than was at first suspected. NO is one such case. In the chemical network calculations described above, NO was formed and destroyed by the reactions O(NH,H)NO, N(OH,H)NO, and N(NO,O)N_2. Following the discovery of interstellar NO (Liszt and Turner, 1978), closer scrutiny revealed that N(NO,O)N_2 is impeded by a significant activation energy, and that the reaction of O with NH produces OH but no NO. Models incorporating those revisions predict an NO abundance 10 times lower than predicted by Mitchell et al. (1978), although still somewhat higher than observed. It is also found that the NO abundance actually depends on almost every aspect of the more general nitrogen chemistry, and even upon abundances of metals and of methane.

HCN and NH_3 are two other simple species that initially seemed well predicted by a few dominant reactions but whose chemistry, under continued examination, has grown somewhat more uncertain. HCN appears to have several formation pathways other than via $C^+ + NH_3$, as formerly believed. NH_3 probably forms principally through the species NH_3^+ but the reaction $NH_3^+(H_2,H)NH_4^+$ followed by electron recombination is no longer viable (Watson, 1976), the reaction $NH_3^+(Mg,Mg^+)NH_3$ does not produce observed abundances of NH_3 if metals are seriously depleted (Mitchell, 1978), and the recently proposed reaction $NH_3^+ + H_2 \rightarrow NH_3^+ \cdot H_2 + h\nu$ followed by electron recombination (Huntress and Mitchell, 1979) is now known to be slow. Despite these uncertainties, the observed abundances of HCN and NH_3 are quite well explained in a general sense by the current models. Other observations, such as the higher abundances of HCO^+, HCN, H_2CO (by a factor of 100) in cooler dark clouds as compared with warmer clouds (Wooten et al., 1978) are explained by ion-molecule models, in terms of reduced abundances of electrons and other destructive species.

Large deuterium concentrations have been observed in several small molecules in a few cold clouds (Hollis et al., 1976; Guélin et al., 1977; Turner and Zuckerman, 1978; Snell and Wootten, 1979). These have provided a strong test of the ion-molecule chemistry. The ratios observed, $N_2D^+/N_2H^+ \approx 0.1$, $DCO^+/HCO^+ \sim NH_2D/NH_3 \sim 1$ in extreme cases, even though $D/H \approx 2 \times 10^{-5}$, occur quite naturally from the few ion-molecule reactions that govern these species (Turner and Zuckerman, 1978) provided that the fractional ionization is very low ($\lesssim 10^{-8}$). Even the observed relation $NH_2D/NH_3 \gtrsim DCO^+/HCO^+ > N_2D^+/N_2H^+$ is explained. Further, if the temperature is below the value (~15 K) where metals freeze onto grains, producing an attendant drop in the electron abundance, both the molecular ion abundances, and the fraction that contain deuterium, are predicted to increase sharply, in concert with the observations. Although the reactions involved are less certain, the similar behavior of HCN, HNC, H_2CO, and their deuterium concentrations, strongly suggests that the chemistry of these species is also dominated by ion-molecule reactions. By contrast, no mechanism yet envisioned for surface reactions on grains can produce such large deuterium fractions. Even more indicatively, surface reactions would not produce a higher fractionation in cooler than in warmer clouds, as observed, because surface deuterium-exchange reactions have measured activation energies of ~1000 K (Watson, 1978).

It is not clear to what level of complexity interstellar molecules can be formed by ion-molecule reactions, or gas-phase reactions of any kind. Observations provide no definite clues here, because failure to observe complex molecules in a given source cannot be ascribed with certainty to inadequate chemistry. In fact, since the complex species are seen in only 2 or 3 sources, and those sources are either the hottest or have the largest known column densities of gas, the observed complex species could be a result either of enhanced excitation, or of greater total column abundance. Or, the higher temperatures could imply an altogether different chemistry, such as grain surface chemistry.

Radiative Association Reactions. An important recent advance has been the recognition that the more complex molecules may form at sufficient rates by radiative association. Although very inefficient for diatomic species like CH^+, radiative association becomes much more favorable for larger species with numerous internal vibrational modes. The reaction $C^+ + H_2 \rightarrow CH_2^+ + h\nu$ has been much studied theoretically, as it may be the major starting point for interstellar hydrocarbon chemistry. Radiative association has also been proposed for the formation of polyatomic species, up to 12 atoms (Millar and Williams, 1975). Recent laboratory work gives some support to the large theoretical rates of these large-fragment associative reactions. It is found (Smith and Adams, 1977, 1978) that associative reactions of CH_3^+ with several known interstellar species containing up to 7 atoms proceed rapidly with rates that may even exceed gas-kinetic rates at low (20-50 K) temperatures. Expected products contain up to at least 10 atoms and explain the presence of several of the most complex interstellar molecules as well as others not yet detected. Associative reactions with CH_3O^+, CH_5^+, HCO^+ and other small ions have also recently been considered (Huntress and Mitchell, 1979). These additional reactions are not yet supported by laboratory experiment, but appear capable of effectively synthesizing a large number of the complex interstellar species presently observed, and many others besides. As the rates grow larger with increased size, one may even speculate that rapid associative reactions (condensations) gradually produce very large condensates which will eventually build into 'dust grains' whose composition would then be agglomerates of solid water, alcohols, aldehydes, etc. (Smith and Adams, 1978).

Possible Limitations of Ion-Molecule Reactions. While ion-molecular processes have had unparalleled success so far in understanding interstellar chemistry, they are not without possible difficulties. One problem is CH^+. Formation of CH^+ via diatomic radiative association is too slow in comparison with the destruction reaction $CH^+ + e \rightarrow C + H$, and formation of CH^+ via $C^+ + H_2 \rightarrow CH_2^+$ cannot produce the observed CH^+/CH ratio in diffuse clouds, regardless of the adopted rate, which is very uncertain. Elitzur and Watson (1978) have recently shown that adequate amounts of CH^+ (and CH) can be formed in diffuse clouds via the endothermic process $C^+ + H_2 \rightarrow CH^+ + H$ but only under conditions of high transient temperatures in shocks. Another problematic species is H_2CO. Models predict observed abundances for denser clouds but fall well short for diffuse clouds (Millar and Williams, 1975a; Davies and Matthews, 1972). The problem is that all postulated formation pathways involve a radiative association step which competes unfavorably with the photodestruction rate of H_2CO in any but optically opaque clouds. The long-chain cyanopolyynes are another possible difficulty for gas-phase chemistry. HC_3N cannot be formed at sufficient rate by the reaction $C_2H_2^+ + HCN$ (Huntress and Mitchell, 1979). Further, the continuation to longer chains HC_nN, $n \geqslant 5$, cannot occur via $C_2H_2^+ + HC_3N$, which has been measured by Freeman et al. (1978) to have a negligible rate; similarly reactions of protonated HC_3N with suitable hydrocarbons also fail to increase the length of the carbon chain. The recent discovery of HC_5N and HC_7N in the circumstellar shell surrounding the evolved star IRC+10216 (Winnewisser and Walmsley, 1978) suggests at least that mechanisms other than ion-molecule reactions can form long-chain molecules, since the species HCO^+ and N_2H^+, which are signatures of ion-molecule processes, are not seen in IRC+10216. Certain other key ions predicted by ion-molecule schemes, such as $HCNH^+$ and HCO_2^+, have not yet been detected in molecular clouds, presumably because transition frequencies for these species are not precisely known (although the uncertainties are not likely greater than were those of HCO^+ when it was first identified). Finally, an explanation for the rarity of N-O bonds among polyatomic interstellar molecules has not yet emerged in terms of gas-phase reactions.

III. Grain-Surface Reactions

Basic Principles. The four important processes in all models of surface reactions are adsorption of a radical or atom from the gas, its migration over the grain surface via quantum-mechanical tunneling, its reaction with a second adsorbed atom or molecule, and ejection or evaporation of the product molecules back to the gas phase. The details of each of these processes depend critically on the temperature, composition, and physical properties of the grain surface. As the roles of the composition and surface properties have not yet been elucidated in detail in the laboratory, it is understandable that interstellar surface chemistry has received less attention than gas-phase chemistry. A few rather definite statements can be made about interstellar surface chemistry, however: (a) interstellar H_2 is formed primarily on grains (see, e.g., Watson, 1978) but requires grain temperatures to be less than $\sim$22K;(b) even in cold clouds, the rate of incidence of gas particles upon grains is comparable, if not greater than, gas-phase ion-molecule rates, and exceeds most radiative association rates; (c) the probability of the incident particle sticking to the grain is of order unity for 'heavy' atoms or radicals and probably not less than $\sim$0.2 for H atoms, even on the most unfavorable surfaces (based on laboratory experiments). Ample observational evidence now exists (Jura, 1976; Crutcher, 1976; Jura and York, 1978) that grains selectively adsorb heavy atoms, and cause the selective and variable depletion of the heavy refractory elements (Fe, Mg, Si, Ca, etc.) seen in molecular clouds; (d) in *cold* clouds ($T_{grain} \leqslant 20$ K) the binding energy to grains of saturated molecules, and probably also of atoms and radicals will be weak, corresponding to physical adsorption. The reason is that even if grains do not initially contain ice mantles or low-binding mono-layers of H_2, they will soon accumulate them. On initially more strongly binding surfaces, evaporation is not possible, so condensation of H_2 or of ices of H_2O, NH_3, CH_4 will occur, on top of which the binding is weak; (e) in *warm* clouds, where IR observations indicate grain temperatures are often 40-80 K, ice mantles or H_2 layers will evaporate, surfaces will be chemically active, and atoms or radicals will bind tightly. Saturated molecules will still be only weakly bound.

In order to incorporate these ideas into a convincing scheme for forming interstellar molecules, we require answers to several questions. (1) Is the heat of formation adequate to eject newly formed molecules from grain surfaces? The answer is likely yes for physically adsorbed saturated species, no for chemically adsorbed atoms and radicals (except possibly for very small grains), but uncertain for physically adsorbed atoms and radicals, and for semi-chemically adsorbed saturated species on active surfaces. In some cases experimental evidence allows educated guesses. (2) Are activation barriers generally small enough to permit surface reactions, and are there significant differences in these barriers, and in surface mobilities from one species to another? Generally, activation barriers are likely sufficiently small between atoms or radicals, but not necessarily between a radical and a saturated species, and not between saturated species. Mobilities definitely depend on species, based on limited data. (3) Are there alternative (non-thermal) ejection mechanisms for newly formed surface molecules? Watson (1978) has analysed several possibilities, including photodesorption, thermal pulses in small grains, and shock waves. Based on laboratory experiments, photodesorption in diffuse clouds would appear to proceed at adequate rates but just what molecules or molecular fragments are desorbed would be difficult to predict. The same statement can be made about desorption by sputtering, as occurs in shocks. There are strong arguments against desorption by thermal pulses, as initiated by photons, cosmic rays, or energy of recombination (Watson, 1978).

Some detailed calculations of interstellar molecular abundances expected as a result of grain synthesis have been made (Watson and Salpeter, 1972; Allen and Robinson, 1977; Iguchi, 1975). The results of these studies are highly varied, as may be expected from the very different assumptions made. None of the results matches the observational picture very well in general, nor appears capable of the degree of specificity needed to describe, for instance, the different relative molecular abundances found in the cold vs. warmer molecular clouds. Iguchi (1975) does present evidence that the mobilities of N and O atoms, or of small molecules containing them, are less than for C atoms or small C-molecules on grain surfaces that contain ice mantles. If so, then molecules containing N-O bonds would be less readily formed than those in which C-bonding predominated. On this picture, the presence of NO itself but not of larger saturated N-O bonded molecules like NH_2OH would imply that NO is formed in the gas phase, because the binding of unsaturated species like NO on cold grains would exceed that of saturated species like NH_2OH. Further, if grains were *generally* involved in forming interstellar molecules, then the absence of species like NH_2OH coupled with the presence of species like CH_3OH would suggest that most if not all saturated molecules containing 5 or more atoms are formed on grains. Since this is the level of complexity at which gas-phase reactions are also becoming highly uncertain, it is hard to assess the merits of this hypothesis.

Difficulties for Grain-Surface Chemistry: Diffuse and Cold Clouds. In diffuse clouds, where atomic hydrogen is abundant, it impinges on grains at about 1000 times the rate of C,N,O atoms. Under conditions near physical adsorption, where surface mobilities are unrestrained, hydrides should be formed predominantly over other species on grain surfaces. In particular, NH and OH should form about equally per atom (Watson 1978) so that if the optically observed OH in diffuse clouds is produced on grains, then NH should be present in moderate abundances. A search for NH (Crutcher and Watson, 1976) gives $NH/OH \lesssim 0.01$. This result does not auger well for surface chemistry dominating at the diatomic level, although the fact that $N/O \approx 0.14$ as well as other uncertainties do not allow ruling out grain reactions at this level.

The long-chain molecules HC_nN are a particularly intriguing possibility to distinguish grain from gas-phase chemistry. Among interstellar clouds, they are observed only in two small, nearby regions in Taurus. Their rare occurrence does not point to a unique chemistry in Taurus, however, for the sizes of the HC_nN regions are very small (Little et al., 1978) and would be undetectable if much farther away. A large DCO^+/HCO^+ ratio has been detected in the HC_nN region (Langer et al., 1978) which, according to the ion-molecule picture of these ions, implies very low electron and CO fractional abundances, and suggests that the grains are so cold ($\lesssim$ 15 K) that metals and CO freeze out (Turner and Zuckerman, 1978). Such unusually cold grains would seem very unlikely sites upon which to form and eject such highly unsaturated species as HC_nN. It is of interest that no changes in OH abundance are seen in the region of the HC_nN sources (Turner et al., 1979). This result is consistent with gas-phase chemistry models for OH if the density increases from $\sim 10^3$ outside to $\gtrsim 10^4$ cm^{-3} inside the HC_nN region, as suggested by the large DCO^+/HCO^+ ratios observed here. Failure to observe the HC_nN species in a few other nearby dark clouds that also exhibit large DCO^+/HCO^+ ratios and physical conditions similar to those in the Taurus cloud, may imply a different elemental composition for the Taurus cloud gas, if we are to explain HC_nN by gas-phase processes. This would be consistent with the OH behavior, as the OH chemistry is shown (Mitchell et al., 1978) to be particularly insensitive to composition and temperature.

As we have seen, several small molecules (HCN, HNC, CO, H_2CO) are observed to have higher relative abundances in cold dark clouds than in warmer clouds (Wootten et al., 1978). This circumstance is readily explained by gas-phase ion-molecular processes in terms of lower ionization fractions in the cold clouds, as are the larger deuterated ratios seen in these clouds. But it is counter to expectations for surface chemistry. H_2CO is therefore probably formed by gas-phase processes, even though suitable ones have not yet been found. The recent detection (Langer et al., 1979) of HDCO and the large $HDCO/H_2CO$ ratio observed in two cold clouds are even stronger arguments that H_2CO is formed in the gas phase. More complex molecules are not generally detected in cold clouds so one cannot argue for or against their formation on grains, on these grounds.

Prospects for Grain-Surface Chemistry in Warm Clouds. Evidence for or against surface chemistry in warm clouds is sparse. Here, the grains are not covered with ices, and their basic composition becomes relevant. Absorption features in the IR spectrum in the 2-20 μm region have long suggested a composition mainly of silicates. Another traditional candidate is graphite grains, or grains with mantles of organic molecules (cf. Hoyle and Wickramasinghe, 1976). Combinations of graphite particles and silicates of Fe and Mg have been shown by Mathis et al. (1977) to match the interstellar extinction law over the entire range $0.11 \leqslant \lambda \leqslant 1$ μm. Duley and Williams (1979) have recently suggested that the absence of a C-H vibrational transition at 3.3-3.4 μm in the spectra of several objects implies that less than 1% of a cosmic complement of carbon in grains can exist as organic molecules. However, more recent data (Willner et al., 1979) reveal a weak feature at 3.4 μm toward the galactic center, which is attributed to CH_2 or CH_3 groups within the grain surfaces. A third possibility is small ($<$ 100 Å) grains composed of metallic oxides (Millar and Duley, 1978). Such grains appear able to deplete selectively certain elements (Fe, Mg, Ca, Al, etc.) in accordance with the observations (Duley and Millar, 1978).

Some experimental data exist about what types of molecules may be synthesized on these types of grains. (a) *Silicate surfaces.* According to experiments by Anders et al. (1974), a large variety of organic molecules can be catalysed on silicate surfaces, at temperatures of $\sim$500 K, including probably the HC_nN species (not yet observed in warm clouds). These Fisher-Tropsch type reactions are inoperative at the much lower temperatures of warm interstellar clouds, but may well be productive in the proto-solar environment of the early solar system and of other forming stars. These reactions predict a fall-off in abundance with increasing number of carbon atoms that appears much steeper than observed in the interstellar species. This, and the failure to detect many other species predicted to be abundant, suggests that at least the 'protosolar nebulae' cannot have ejected enough material into the surrounding interstellar cloud to alter its molecular composition significantly. (b) *Graphite grains*. Experiments at 78 K using graphite surfaces (Bar-Nun, 1975) show that CO, CO_2, and hydrocarbons are synthesized from reactions of H, N, O, and S. A carbon atom is removed from the graphite for each molecule formed, a process that would soon erode away interstellar grains, which at least in cool clouds seem to accrete with time (Carrasco et al., 1973). Graphite synthesis might in principle be significant in warm clouds near HII regions, but predicted distributions of H_2CO and hydrocarbons in a thin shell around HII regions (Barlow and Silk, 1977) are not observed. Grain lifetimes would be only $\sim 3 \times 10^5$ years, much shorter than cloud lifetimes. Graphite grain synthesis can be expected to operate in the protosolar environment, but, again, this would be unlikely to affect molecular abundances in the associated interstellar cloud. Barlow and Silk (1977) believe, however, that all of the solid material in the solar system originated as interstellar dust, was not vaporized, and that any graphite component was mostly converted by grain surface reactions under protosolar conditions into the organic molecules now found in carbonaceous chondrites. (c) *Metallic oxide grains*. Alkaline-earth oxides are well known chemical catalysts. Based on experiments at ~77 K, Duley et al. (1978) have modelled the active sites on MgO/FeO/SiO/CaO grains. In *diffuse* interstellar clouds these sites are maintained by UV and cosmic rays, and can apparently form molecules such as H_2O, HCO, NH_3, H_2CO with high efficiency. Ejected by the heat of formation, these species are rapidly photodissociated to form CO, OH, NH. The observed limit on the NH/OH ratio poses a difficulty for this model as it did for the more general considerations mentioned previously. However, the large observed abundance of H_2CO in diffuse clouds, a current difficulty for gas phase reactions, might be possible through formation on such surfaces (Millar et al., 1979). In *dense* clouds the active surface sites of oxide grains appear to become poisoned and at best might form only molecules with several heavy atoms (Duley et al., 1978). Such molecules apparently cannot be released to the gas. Thus it appears that oxide grains are more likely to account for depletion of the elements than for production of gas-phase molecules.

Ring compounds have not yet been detected in interstellar space. It is believed that gas-phase processes, either ion-molecule (Fertel and Turner, 1975) or radiative association (Millar and Williams, 1975b) are incapable of producing ring compounds under interstellar conditions, whereas surface reactions would not necessarily discriminate against them. Thus the failure to observe rings has been used as an argument against surface chemistry even in warm clouds. However it can be argued (Leitch-Devlin et al., 1976) that the expected abundance of simple ring compounds produced by grain surfaces would be well below the current detection limits for these molecules. Eventually, the detection or otherwise of ring species should provide a definite test for interstellar surface chemistry.

Diffuse Interstellar Bands. The origin of the diffuse interstellar bands remains unsolved. Although traditionally attributed to effects within grains or to molecules embedded in grain surfaces [see, e.g., Duley and McCullough (1977) for a recent model], current observational results (Snedden et al., 1978) indicate that at least the grains responsible for visual and IR extinction may not be the carriers of the diffuse bands. Douglas (1977) has recently suggested a mechanism by which the broad lines ('bands') can be produced by gas-phase molecules, and proposes carbon-chain molecules as the specific carrier. Huntress and Mitchell (1979) have suggested how long-chain hydrocarbons can be built up by ion-molecule reactions in dense molecular clouds. This idea is not based on measured reaction rates, and would be inoperative in diffuse clouds owing to the larger fractional abundance of charged particles, which destroy the hydrocarbons upon collision. Therefore a potential difficulty is in ejecting sufficient quantities of the hydrocarbons from the cold dense clouds into the more widespread diffuse regions where the diffuse bands are observed. Also noteworthy is that neither propane nor propylene, both predicted by this model, have been detected. If diffuse bands really come from long-chain molecules, a surface chemistry might be indicated owing to the difficulty in building up chains in the gas phase from smaller molecules which would be dissociated very quickly in the diffuse interstellar radiation environment. Carbyne chains have been suggested as an important constituent of grains (Webster, 1979), from which HC_nN molecules would be expected to be easily formed.

Summary. We may summarize the prospects for interstellar grain chemistry as follows. Grain chemistry can be expected to be important in shock regions where grains are directly sputtered, and may possibly contribute to the rich molecular composition of the most prominent sources. Grain processes which occur in protosolar regions are unlikely to affect the overall molecular composition of the cloud in which they are embedded. Surface chemistry could be important in situ in warm molecular clouds, but may destroy the grains in the process (if they are graphite). No observational evidence is available to decide this point directly, or to accept or reject grain chemistries in warm clouds on the basis of expected products. However, the few difficulties encountered at present by gas-phase models of interstellar chemistry are not alleviated by invoking grain surface reactions, except possibly the apparent lack of N-O bonds among larger species. Additional lines of observational evidence argue against the importance of surface reactions at least in cold clouds.

IV. Shock Chemistry

Shock fronts occur at the interface of expanding HII regions or supernova remnants and the surrounding dense neutral gas. They have recently received much attention as a mechanism for triggering gravitational instabilities and the onset of star formation (Elmegreen, 1977; Elmegreen and Lada, 1977; Elmegreen and Elmegreen, 1978). A typical HII/HI shock moves into a molecular cloud at 10 km/s, inducing a sudden jump in the gas temperature from $\sim$30 K to typically 3000 K and a jump in the density of about 6-fold just behind the shock. As the compression front moves on, the gas cools, first by rotational-vibrational excitation of H_2 ($T > 500$ K) and then by rotational excitation of CO ($T < 500$ K). Constant pressure is maintained, so the density increases further as the gas cools, by perhaps another factor of 10. The time scale for the gas to cool completely is several hundred years and the size of the region over which temperatures are enhanced is $\sim 10^{15}$ cm.

Many gas-phase reactions become important in the post-shock region that do not normally operate in molecular clouds, namely neutral-neutral reactions that are endothermic, or that are exothermic with activation energies. As many more of these reactions have been studied than have ion-molecule reactions, it is presently a matter of taste as to what reactions are included in chemical network calculations. Iglesias and Silk (1978) include the usual ion-molecule reactions and 46 additional reactions involving H, C, N, O whose reaction times are less than the cooling time behind the shock. Hartquist et al. (1979) omit ion-molecule reactions as being too slow and include 29 reactions involving H, C, O, S, Si in order to assess the S, Si chemistry. Elitzur and de Jong (1978) include 18 reactions involving C, O, H in order to study OH chemistry associated with OH/H_2O masers.

Ion-molecule schemes seem able to explain the observations of OH, and of sulfur and silicon species in normal molecular clouds (Oppenheimer and Dalgarno, 1974; Turner and Dalgarno, 1977; Mitchell et al., 1978). If the OH abundance in OH maser regions is much higher than in normal clouds, as appears likely, an alternative such as shock chemistry may be required. In some objects the emission of the S and Si species has unusually broad line shapes and is spatially more restricted than are other species. These attributes suggest that the S and Si species are formed in shocks in these sources; the shock chemistry described above also explains the observed abundances in these cases, which are many times higher than in most sources. Current shock-chemistry models predict that abundances of some species are not affected noticeably by the shock, among them CO and HCN. Therefore the broad line profiles emitted not only by the S and Si molecules but also by HCN in a few sources may imply needed modifications to the models.

The overall applicability of shocks to interstellar chemistry is probably restricted to regions of bright nebulosity and star formation. The interstellar medium is pervaded by weak shocks generated by old supernova remnants and by spiral density waves, but shocks strong enough to alter the chemistry probably occur only in the vicinity of young HII regions and supernovae. Nonetheless, more than two-thirds of the presently observed interstellar molecules, including almost all of the more complex species, are seen *only* in the Sgr B2 and Orion molecular clouds, objects which also exhibit evidence of shocks. Sputtering of molecules from grains is also a likely process in shocked regions, although it has not been possible to predict meaningfully what molecular products should result from this process. Clearly much more extensive calculations are needed of the chemical processes in shocked interstellar gas, to assess whether shocks are an overall important aspect of interstellar chemistry.

V. Isotope Ratios in Interstellar Molecules

The relative degree to which various isotopes make their appearance in interstellar molecules may or may not reflect closely the corresponding nuclear isotope ratio in the interstellar gas. A measurement of similar values for a given isotope ratio in different molecular species, especially when supported by reasonable chemical arguments, is taken to indicate that that particular ratio is not subject to chemical fractionation or 'concentration', and accurately represents the isotope ratio in the overall gas. In this way, one concludes that fractionation does not affect much the ratios $^{15}N/^{14}N$, $^{18}O/^{16}O$, $^{17}O/^{16}O$, $^{34}S/^{32}S$, $^{33}S/^{32}S$, $^{29}Si/^{28}Si$, and $^{30}Si/^{28}Si$ as they appear in molecules. The ratio $^{13}C/^{12}C$ is somewhat affected. The ratio D/H is profoundly affected by the chemistry, sufficiently so that one cannot hope to derive from molecules any cosmologically useful information about the atomic D/H ratio in the gas. That deuterium should be so strongly affected follows from the large mass ratio of D/H, which results in a difference in vibrational energy for D in H_2 and in larger molecules such as HCN of about 300 cm^{-1}. By contrast, the difference in vibrational energy of ^{13}C and ^{12}C in various molecules is only about 10 cm^{-1}, and is even less for isotopes of O, N, S, and Si. By scaling down the observed D concentration in accordance with the energy differences, we would conclude that fractionation is unimportant for the other elements except possibly for carbon.

The D/H Ratio. In the local regions of the galaxy (out to 2 kpc) the atomic D/H ratio has been measured directly as 2×10^{-5} from the UV lines of the respective atomic species. Models of the big-bang origin of the universe relate the 'primordial' D/H ratio to the present-day mass density of the universe in such a way that if primordial, the observed value for D/H would correspond to a mass density of 4×10^{-31} gm/cm^3, insufficient by two orders of magnitude to close the universe. Unfortunately, since D is selectively destroyed by processes of astration - nuclear burning in stars - and may also be created by other astrophysical processes such as supernova explosions, it is unclear how well the observed D/H ratio reflects the primordial ratio. One way to decide is to look for a gradient in D/H across the galaxy. The idea is that the astration rate (rate of nuclear processing in stars) is known to increase faster in the galactic center than does the number of supernovae, so that an observed decrease in the D/H ratio in the galactic center would indicate that the net effect of stellar activity is to destroy rather than to create deuterium. Then the observed local D/H ratio would be an upper limit to the primordial ratio, indicating an open universe. (One has still to calculate the relative effects of astration and of supernovae on the D/H ratio locally, but here the space density of stars of all types is well known. The conclusion is that locally the effects of stars on the D/H ratio has been small over the history of the galaxy, and that the observed ratio departs by a factor of only 2 to 4 from the primordial value.) These arguments have been well summarized previously by Penzias (1978) and by Ostriker and Tinsley (1975).

Because observations in the UV can penetrate only a small distance through the galaxy, information on a galactic gradient of D/H has come solely from observations of molecules at mm-wavelengths, which can penetrate the entire galaxy. It is found that the abundances of *all* deuterated molecules so far observed are smaller relative to their non-deuterated counterparts in the galactic center than elsewhere in the galaxy. The insensitivity of this result to the particular molecular species has been argued by Penzias (1978) to imply a real reduction in D/H in the galactic center, rather than a difference in the chemistry there.

The degree of deuterium-concentration in observed interstellar molecules is enormous, ranging from factors of ~200 in typical warm clouds to $\gtrsim 10^4$ in the cores of some cold clouds. As we have seen, these large deuterium-concentrations are a natural prediction of ion-molecule reactions (Watson, 1976; Guélin et al., 1977; Turner and Zuckerman, 1978). In this type of chemistry, the degree of D-concentration varies roughly inversely as the fractional electron abundance, which in turn is lower in the coldest clouds where metals freeze more efficiently onto grains. This result suggests an alternative explanation to the cosmological one of why molecules exhibit less deuterium in the galactic center. Because processes of astration are more advanced in the galactic center, the metal abundance is higher there than elsewhere in the galaxy. Higher metals mean higher fractional electron abundances (because metals compete, by charge exchange, with electrons in neutralizing molecular ions), and thereby lower deuterium fractionation. Despite their failure to clarify the cosmological problem, studies of deuterated molecules have provided possibly the best quantitative test of ion-molecule chemistry so far; they have also been the most sensitive probe of ionization conditions in opaque clouds, and have given the currently most stringent upper limit on the galactic cosmic ionization rate, $\lesssim 10^{-18}$ mol^{-1} sec^{-1} (Wootten et al., 1978; Turner and Zuckerman, 1978).

Other Isotope Ratios. The relative abundances of isotopes of C, N, O, S in interstellar molecules are better determined than is the D/H ratio. Unlike the D/H ratio, they do not differ greatly from the atomic ratios in the solar system, although the small departures that do exist have important implications about the nucleosynthesis history of the galaxy.

Starting with the 'primordial' elements H and He, nuclear processing in stars forms the heavier elements and their isotopes through continued cycling between stars and interstellar gas. The concentrations of these elements in the gas as a function of time depend on the rates of star formation, the stellar mass distribution, nuclear processes within the stars, and the rates of re-emission of stellar material back into the interstellar medium. Detailed calculations of these processes (Vigroux et al., 1976) show that the common isotopes ^{12}C and ^{16}O are formed first, and ^{13}C, ^{17}O, ^{18}O, ^{14}N, ^{15}N are formed from them by secondary processes. All grow in abundance with time. For fast rates of stellar processing appropriate to the galactic center, the $^{12}C/^{13}C$ ratio decreases with time to a steady value of ~20 after 5 x 10^9 years. For slower rates of stellar processing characteristic of the galactic disk, the $^{12}C/^{13}C$ ratio is expected to decrease more slowly, reaching ~90 when the earth was born 4.8 x 10^9 years ago, and ~60 at the present age of the galaxy (~8 x 10^9 years). More recent calculations (Dearborn et al., 1978), incorporating revised theoretical nuclear burning rates, indicate that even smaller differences between the terrestrial and galactic disk values of $^{12}C/^{13}C$ may be expected.

The observational situation regarding the isotopes of C, N, O, and S was discussed by Townes (1977, 1978) who drew 4 major conclusions about the important $^{12}C/^{13}C$ ratio: (a) the same value is derived from CO and from H_2CO, indicating that chemical fractionation of these isotopes is unimportant; (b) a mean value $^{12}C/^{13}C \approx 50$ is found for the galactic disk; (c) there are real variations in the $^{12}C/^{13}C$ ratio from cloud to cloud within the galactic disk. Townes believed that the difference between the mean disk value of 50 and the terrestrial value of 89 was larger than could be explained by the ratio of ages of the earth and galaxy, and that some revision in our understanding of the nucleosynthesis history of the galaxy was necessary. He also concluded from variations of the $^{12}C/^{13}C$ ratio among clouds that cloud lifetimes must be very long, ~10^9 years, in order for these variations to have a chance to build up.

More recent data on the $^{12}C/^{13}C$ ratio have been obtained from H_2CO (Henkel et al., 1979), HC_3N (Wannier and Linke, 1978), and NH_2CHO (Lazareff et al., 1979). When H_2CO observations are properly corrected for opacity effects, revised values result for the $^{12}C/^{13}C$ ratio as deduced from H_2CO, which no longer agree with those derived from CO, but are typically larger. Such a conclusion is confirmed by a comparison of the 'double ratios' $H_2{}^{12}C^{18}O/H_2{}^{13}C^{16}O$ and $^{12}C^{18}O/^{13}C^{16}O$ which differ by a factor of over two even though opacity effects must be unimportant in these rare isotope species. An average galactic disk value for $^{12}C/^{13}C$ is 68 derived from H_2CO and 38 derived from CO. Fractionation of the ^{13}CO is clearly indicated. A mechanism for such fractionation was proposed several years ago by Watson et al. (1976) based on the reaction $^{13}C^+ + {}^{12}CO \rightarrow {}^{13}CO + {}^{12}C^+$ which is exothermic by 35 K, as shown. Together with the preferential freezing out onto grains of organic molecules *other* than CO (which has an unusually high vapor pressure), this reaction leads to a net decrease in the $^{12}C/^{13}C$ ratio in the gas. Hence molecules other than CO should exhibit a higher $^{12}C/^{13}C$ ratio in the gas phase than does CO itself, a conclusion which is borne out by the observations. One may therefore take the $^{12}C/^{13}C$ ratio derived from H_2CO as a best estimate, in which case the mean value for the galactic disk, $\sim$68, is probably consistent with the currently understood nucleosynthesis history of the galaxy, especially if some ^{13}C fractionation occurs in H_2CO also. Furthermore, apparent variations in the $^{12}C/^{13}C$ ratio from cloud to cloud are easily explained by differing degrees of fractionation (due to differing termperatures), and do not imply differences in nucleosynthesis timescales that suggest long cloud lifetimes.

In the galactic center, a ratio $^{12}C/^{13}C \approx 20\text{-}25$ is derived now from 4 different molecular species: CO, H_2CO, HC_3N, and NH_2CHO. This consistency, despite different chemistries for each species, suggests a real enhancement of ^{13}C in the galactic center. The value 20-25 for the $^{12}C/^{13}C$ ratio agrees well with the predictions of nucleosynthesis for the galactic center region, as described above. Observed increases in the relative abundances of ^{17}O and ^{18}O, together with a decrease in ^{15}N, are also consistent with the advanced nucleosynthesis picture of the galactic center.

VI. Interstellar Molecules and the Molecular History of the Solar System

Protosolar Nebulae as Sources of Interstellar Molecules. Until recently the relationship between interstellar molecules and the early solar system (or protosolar nebulae in general) was viewed in terms of protosolar nebulae supplying molecules to the interstellar medium (Herbig, 1970; Anders et al., 1974). Several arguments suggested this hypothesis. It is known that stars of mass $\lesssim 1.5$ solar masses exhibit only little angular momentum, implying that this momentum has been transferred to a primordial stellar disk. Further, all volatile elements complementary to the inner planets (amounting to about 0.003 solar masses) have been lost from the solar system (possibly as a result of a flareup of the sun while in an early T-Tauri phase). For example, the earth retains only 10^{-4} of its cosmic complement of carbon, and even less water, nitrogen, and noble gases. The remaining carbon exists largely in the form of molecular products of Fischer-Tropsch type (FTT) reactions, which, along with conditions expected in the presolar nebula, suggests that these molecules were also the form in which gas was lost to the interstellar cloud in which the sun formed.

It is through the study of the embedded molecular constituent of meteorites (carbonaceous chondrites) that much has been learned about conditions in the presolar nebula. The currently accepted picture (cf. Anders et al., 1974) is as follows. At an appropriate stage in the solar nebula, whose lifetime was about 10^4 years, gas densities were typically 10^{14} H_2 molecules cm^{-3}, temperatures were several hundred K, and there was abundant particulate matter, mostly in the form of silicate grains. The carbonaceous chondrites, containing carbon mostly in the form of organic compounds, and now generally agreed to represent low-temperature condensates from the solar nebular gas, formed at temperatures of 360-400 K. The time scale for the entire evolution of carbonaceous chondrites, from condensation through chondrite formation and accretion to end of metamorphism in the parent bodies was $(2 \pm 2.4) \times 10^6$ years. The organic compounds in the chondrites were formed via FTT reactions of CO (the stable form of carbon at high temperatures) on grains of silicates and magnetite, which are effective catalysts; the reaction time constant was about 500 years, much less than the solar nebular lifetime. Experiments simulating these conditions (Anders et al., 1974) find good agreement between the molecular composition of the chondrites and the products of FTT reactions.

Interstellar molecules do not bear a compositional similarity with the products of FTT reactions (§III). But this does not argue strongly against the above picture. At a distance of ~100 pc (that of the nearest interstellar clouds containing solar-like stars) a presolar nebula 3 times the size of the present solar system would be underresolved by a factor of 100 with current radio telescopes. On the other hand, only 33 stars (typical of the number of T-Tauri stars in many dark clouds), each losing 0.003 solar masses of volatiles, would contribute 0.1 solar masses of organic molecules, or roughly the amount actually observed in dark clouds of 1000 solar masses. The failure to detect these FTT molecular products is not likely the result of insufficient dispersal throughout the cloud, but may result from subsequent chemical modification of the FTT products in the interstellar cloud. Current observations suggest, however, that protosolar nebulae have at most a very small effect on the overall molecular chemistry of interstellar clouds.

The Influence of Interstellar Molecules on Protosolar Nebulae. The inverse question, whether interstellar molecules and grains play a significant role in the molecular history of the solar system, has recently received new attention. In principle, such a role can come about either as a result of interstellar grains surviving intact in the early protosolar nebula, and subsequently influencing the molecular chemistry of the solar nebula, or by interstellar molecules themselves arriving in significant quantities in the protosolar nebula, most likely as mantles of organic material coating interstellar grains.

With regard to the first of these possibilities, it is known that carbonaceous chondrites contain inclusions of graphite along with those of silicates covered with the organic products of FTT reactions. Unlike the silicates, graphite cannot condense out of the hot protosolar nebular gas when the C/O abundance ratio has the solar system value of 0.55. Thus Barlow and Silk (1977) have suggested that at least the graphite, if not all solid material in the solar system, originated as interstellar grains which were not vaporized by the early hot (2000 K) phase of the solar nebula. The high temperatures permit surface reactions of H, N, O, C to occur rapidly on the graphite grains, forming simple molecules which then are converted via FTT reactions on nearby silicate grains to complex molecules. Under these high temperatures, the graphite does not lose C-atoms during surface reactions, so that the graphite survives and is subsequently clumped into aggregates with silicate grains and preserved as inclusions in meteorites. Further, the synthesized molecules have the $^{12}C/^{13}C$ ratio of the protosolar gas and not the much lower ratio expected for the graphite if it is originally formed in the atmospheres of evolved carbon stars. This picture of the early molecular history of the solar system does not lead to results differing from those of the Anders et al. (1974) model, although it does circumvent a possible difficulty of the Anders model, namely whether the CO needed to initiate the FTT reactions can really survive metastably to temperatures as low as 400 K where carbonaceous chondrites formed. The Barlow and Silk picture also implies that protostellar nebulae are not a source of new interstellar grains or molecules.

The second possiblity is that interstellar molecules arrive in the solar system embedded in grain mantles. Can interstellar organics really reside in significant quantities in mantles covering interstellar grains? This question has recently been considered at length, but without a definite conclusion. Interstellar molecules certainly freeze onto grains in cold clouds, and the more volatile of these molecules (e.g., ices) certainly evaporate again if the cloud is heated by embedded protostars (§III). Some organics might possibly not evaporate, especially if they exist on grain surfaces as complex, organic solids which may be sticky or tar-like. Sagan and Khare (1979) have proposed that such complex organic material ('tholins') which they produce experimentally by UV irradiation or sparking of mixtures of simple interstellar molecules, does indeed coat interstellar grains. Since these sources of energy do not exist in dense interstellar clouds, Sagan and Khare envision that the grain/tholin particles are formed and ejected by either protosolar nebulae or evolved (red giant) stars. Evolved stars may be rejected on grounds of the $^{12}C/^{13}C$ isotope ratios and the problems of traversing unshielded regions of interstellar space (§I). Protosolar nebular sources of tholins imply that tholins should also be present in carbonaceous chondrites. Evidence based on infrared spectra and chemical analysis shows definite differences between tholins and chondritic material, but does not rule out some tholin material within chondrites. An alternative origin for organic polymers on interstellar grains, proposed by Hoyle and Wickramasinghe (1976) is that interstellar molecules which freeze onto grains in turn form polymeric mantles, the precise composition of which is uncertain. Refractory grains with such tar-like polymeric coatings will tend to stick to one another as they collide, forming 1 μm-sized agglomerates, such as found in carbonaceous chondrites, in a time of about 10^6 years. Incorporated into presolar nebulae, these grain agglomerates might serve as accretion sites for chondrites and eventually even planetesimals. With only a minor degree of metamorphism, such grain clumps would, according to Hoyle and Wickramasinghe, resemble the chemical makeup of the chondrites.

There is little evidence that can test these speculations at present, but there are potential problems. Lack of suitable energy sources for the production of tholins has been cited already. 'Accretion' theories for organic grain mantles have two difficulties. One is that the lifetimes of interstellar molecular clouds are now believed to be at least 10^8 years, not 10^6 years as adopted by Hoyle and Wickramasinghe, so that accretion would appear to lead to grain aggregates much larger than the sizes found in chondrites. Another possible difficulty is that amino acids such as glycine are abundant in chondrites but are not found in interstellar space. As pointed out by Hoyle and Wickramasinghe, the precursor interstellar molecules HCOOH and CH_2NH, observed in considerable abundance, would be expected to form glycine by a known exothermic reaction.

There is little agreement on whether available infrared spectra of interstellar grains argue for or against the presence of an organic component. Arguments in favor (Sagan and Khare, 1979) cite the observed IR absorption features at ~3 μm and at 8-12 μm which are typical of most or all interstellar sources. A wide range of complex organic mixtures have such absorption features, since C-H, O-H, and N-H vibrational transitions always occur near 3 μm, while the 8-12 μm region is characteristic of C-C, C-O, and C-N groups. On the other hand, Duley and Williams (1979) argue that the C-H stretching vibration should lie between 3.3 and 3.4 μm. Using upper limits for such a feature, which is not observed by Merrill et al. (1976) even in interstellar sources with visual extinction of 50^m, Duley and Williams conclude that no more than 1-2% of the cosmic carbon complement of grains is in the form of organic polymers or various aliphatic compounds, and no more than 10% as aromatic compounds. Whatever the outcome of this issue, two points should be emphasized. One is that the 'typical' interstellar IR adsorption spectrum is characteristic of a wide variety of organic substances, and probably a combination of non-organic materials as well. The other is that there is in fact no such thing as a common IR spectrum characteristic of all interstellar sources. The IR absorption features vary significantly from source to source and, in a few cases, even with time. Because of these two circumstances, no definite composition can be ascribed to grain mantles even if they do contain small amounts of organic matter. In particular, it is clearly unwarranted to suggest the existence of such specific, exotic interstellar substances as polyoxymethylene polymers, polysaccharides (Hoyle and Wickramashinghe 1977a,b) and even sporopollenin (Wickramasinghe et al., 1977).

Although one cannot presently demonstrate a connection between interstellar molecules and the early solar system chemistry, such a connection could have been important in the outer regions of the protosolar nebula (20-30 AU from the protosun) where temperatures probably remained no higher than 100 K. Hoyle (1978) has argued that the protosolar disk would sweep up about 1500 earth-masses of interstellar cloud material, or 1 earth-mass of organic material, in the $\sim 10^7$ years during which the protosolar system was embedded in its placental interstellar cloud. He suggests that planetesimals - icy agglomerates of condensed primordial ices and organic compounds of typical cometary size ($\sim 10^{17}$ gm, 10-100 km) - would form initially. From these the outer planets Uranus and Neptune formed, on a time scale much longer (3×10^8 years) than for the other planets. Many planetesimals were, through interaction, perturbed into a giant halo distribution around the solar system - the so-called Oort Cloud reservoir of comets. Whether the outer planets and comets have chemistries directly related to interstellar chemistry still depends rather critically on what temperatures were reached in the outer protosolar nebula as a result of frictional heating arising from motion through the interstellar cloud. If temperatures exceeded 100 K by much then polymerization or other secondary reactions could have occurred within organic mantles on grain surfaces, or gas-phase molecules could have undergone surface reactions on uncoated silicate, graphite, or metal-oxide grains. A determination of the chemical composition of comets, which so far has met with little success, promises the most direct clues to the early chemical history of the solar system and its relation with interstellar chemistry.

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