

The formation of interstellar

Cosmic rays may provide the energy flux necessary for the continual synthesis of molecules in dense H_2 clouds, according to this detailed model of the carbon, oxygen, hydrogen and nitrogen chemistry of those regions.

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The expanding universe is 10^{10} years old and has a radius of 10^{10} light years or 10^{28} cm. Matter in the universe, distributed in a highly non-uniform manner, is concentrated largely in galaxies, which occupy only a minute fraction (10^{-7}) of the volume of the universe. In addition to stars, most galaxies contain diffuse, low density interstellar matter.¹ Because interstellar matter is most easily studied in our own galaxy, the discussion here will focus on it, although this discussion should be pertinent to other galaxies as well.

The average density of matter in the galaxy is 10×10^{-24} gm/cm³, about half of which is interstellar. If this interstellar matter were uniform in density, this concentration would translate to 3 hydrogen atoms/cm³. However, the density of interstellar material is non-uniform. Specific high-density regions labeled "clouds" range in extent from less than 0.1 to 50 light years² and are irregular in geometric shape. Clouds occupy about 5% of the galactic volume and possess gaseous densities in the range 10 – 10^7 atoms (and molecules) per cm³. In addition, clouds typically contain a particulate component (about 1% of the cloud mass) consisting of dust grains, approximately 0.1 micron in size, whose composition remains unknown. Kinetic temperatures of clouds are (except for ionized, plasma-like regions located near hot stars) in the range 10–100 K. It is generally assumed that the distribution of the various elements is relatively constant throughout the galaxy and, indeed,

throughout the universe.³ A short list of the abundances of some important elements normalized with respect to hydrogen is given in Table 1. If these cosmic abundance ratios apply to interstellar clouds, it is clear that hydrogen, by its dominant abundance, must occupy a unique place in discussions of the chemistry of interstellar matter. The Orion nebula shown in figure 1, for example, has been an extremely profitable source of interstellar molecules.

At this writing, thirty-nine molecular species have been observed in interstellar clouds; they range in size from diatomics to the nine-atom (isomeric) species dimethyl ether ($CH_3)_2O$ and ethyl alcohol (C_2H_5OH). The list of Table 2 shows a richness totally unexpected a decade ago. (The variety of complex organic species observed has even prompted speculations of an interstellar biochemistry!) The vast majority of the molecular species listed in Table 2 has been observed by radio astronomy. The primary reason for this is that for most species, molecular column densities ("column density" is defined as gaseous density $\times$ cloud depth) sufficiently large for observation occur only in the dense interstellar clouds. Because of their dust content, these dense clouds are opaque to visible and ultraviolet light; thus stellar radiation cannot serve as a source for absorption spectroscopy. The details of radioastronomical detection of interstellar molecules are contained in Philip Solomon's article in *PHYSICS TODAY*.⁴ We do note that, for a molecule to exhibit a strong radio or microwave frequency spectrum, it must usually possess a permanent electric dipole moment. The list of Table 2 contains an important bias. Species such as N_2 , CO_2 , CH_4 (methane), and $HCCH$ (acetylene) are non-polar; the question of their abundance or even presence in the inter-

stellar medium is not answered directly by radio observation.

As of several months ago, a number of species listed in Table 2 had not been observed in the laboratory. The astrophysical spectra of these species— HCO^+ , N_2H^+ , CCH , and HNC —were assigned by the help of chemical intuition, isotopic species, fine and hyperfine structure patterns and quantum-chemical calculations (see figure 2).⁵ That these species are not readily observed under laboratory conditions reflects the rather unusual conditions that obtain in the interstellar medium. Within the last few months, R. Claude Woods and his collaborators⁶ have developed a novel experimental technique that has enabled them to do successful radio and microwave spectroscopy of short-lived laboratory species, including ions. This group has already confirmed the spectral assignments of the four unusual species mentioned above, showing that they are indeed present in interstellar clouds. Because radio-astronomical spectra not assignable to previously studied laboratory species are still being observed, the importance of Woods's technique to future identification of interstellar molecules should be emphasized.

Three years ago, Solomon wrote in *PHYSICS TODAY*⁴ that "there is no quantitative theory for formation of polyatomic molecules" in interstellar clouds. Our principal concern in this article will be to discuss a quantitative model for the formation of molecules in the low-density, low-temperature conditions that characterize the interstellar medium.⁷

Lifetimes

To demonstrate the need for relatively efficient molecular formation processes, consider first the expected lifetimes of molecular species in clouds. Many ob-

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molecules

served species have lifetimes of 10^1 – 10^5 years under a wide variety of interstellar conditions. In low density clouds, where appreciable penetration by the general ultraviolet interstellar radiation field occurs, photodissociation and photoionization can be quite "rapid." For example, the radical CH, located in the cloud in front of the star Zeta Ophiucus (gas density 10^2 – 10^3 atoms per cm^3), has a lifetime against photodestruction of only about 750 years.⁸ Even in low-density regions, chemical reaction reduces the lifetimes of molecular species. Take the example of CH just cited; if reaction with the abundant ion C^+ is considered, the CH lifetime is reduced to 500 years.⁸ As the cloud density increases, the time between reactive collisions decreases from millenia and centuries to decades, years, days, and even hours for some especially reactive species. In addition, the volume penetration of galactic ultraviolet radiation decreases; the result is that chemical (collision) processes become dominant in destroying molecular species. To discuss the rates of specific depletion processes in detail at this stage would involve us in the details of the model of interstellar chemistry to be discussed later.⁹ Let it suffice at this juncture to mention the following average predicted⁹ lifetimes against chemical attack for three generic varieties of species in a cloud of gas density 10^5 cm^{-3} :

"inert" neutral species	$\leq 10\,000$ years
"reactive" neutral species	~ 100 years
molecular ions	1 hour–100 years

Despite the uncertainty in all the estimated lifetime figures, it is still difficult to imagine that species will not be destroyed continually in all types of interstellar regions during time periods much shorter than "typical" cloud lifetimes



The Great Nebula in Orion, in which many of the thirty-nine interstellar molecular species observed to date have been identified. The model of cosmic-ray-induced ionization of H_2 and He in dense H_2 clouds, discussed in this article, employs thirty-seven of these molecules in about 100 separate reactions and yields good quantitative agreement with observation.

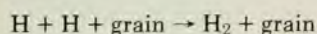
Figure 1

(which are deduced to be not less than about 10^5 years with the assumption of free-fall gravitational collapse²). Possible exceptions are H_2 , CO, and N_2 , with estimated lifetimes greater than 10^6 years in regions opaque to galactic ultraviolet radiation. Consequently, for almost all molecules it is necessary to postulate *continually* occurring formation processes.

Hydrogen

Any discussion of the chemistry of the interstellar medium must commence with a discussion of hydrogen. Because hydrogen is the most abundant reactive element by orders of magnitude, the nature of the chemical processes occurring in a cloud will depend to a considerable extent on what form of hydrogen is dominant. The three major observed varieties of hydrogen are H^+ (H II), H (H I), and H_2 . Ionized atomic hydrogen (H^+) can only occur as an appreciable fraction in clouds close to hot stars. The chemistry of these plasma-like H II regions appears to be limited to atomic species. Collisional processes of interest are those, such as charge exchange, that affect the ionization equilibria of the various atomic species. The boundary between H II regions and H I regions, where atomic hydrogen predominates, is sharp, being of the order of terrestrial dimensions. Outside of H II clouds, there is little stellar radiation left to support the ionization of H; therefore, radiation of wavelength less than 912 Å (13.595 eV) is virtually absent.¹⁰

The boundary between an H I region and an H_2 region (where molecular hydrogen dominates) is also of interest. This boundary can be determined by consideration of the interconversion of atomic and molecular hydrogen. Gaseous H_2 is almost certainly formed from hydrogen atoms by recombination on grain surfaces:¹¹



This reaction is known to occur readily on many surfaces.¹² The unique surface mobility of atomic hydrogen, even at low grain temperatures, coupled with the low grain binding energy of H_2 , causes the $2H \rightarrow H_2$ surface recombination to be orders of magnitude more efficient than any other grain process in producing molecular gaseous species.

Once formed, H_2 can undergo photodissociation by optical radiation via a process that is uniquely interesting. The first allowed optical transition of H_2 , the $B^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ system, has a dissociation limit of 14.67 eV [$D_0^0(H_2) + E_{2s}(H)$]. Thus, H_2 cannot be directly photodissociated by the radiation field present (outside of H II regions) in the interstellar medium. The photodissociation pathway instead consists of a two-step process:

discrete $B \leftarrow X$

bound-bound absorption,

Table 1. Cosmic abundance of the major elements

Relative number abundance	
H	1
He	0.15
C	3×10^{-4}
N	9×10^{-5}
O	7×10^{-4}
Si	3×10^{-5}
S	1.6×10^{-5}

This list is an abridgement from C. W. Allen, *Astrophysical Quantities*, 3rd ed., University of London 1973.

followed by

bound-free $B \rightarrow X$

spontaneous emission

Photodissociation is here caused by *line* rather than continuum radiation. The consequence of this process is that after penetrating a certain H_2 column density, the radiation field soon becomes too weak at the required frequencies to support H_2 line photodissociation. H_2 is then said to be "self-shielded." The relative rates of the two processes—surface recombination and photodissociation—determine the $2H = H_2$ balance. Detailed calculations reveal a relatively sharp boundary between H I and H_2 regions.¹¹

In discussing chemical processes, we consider three rather distinct types of clouds:

- ▶ An H I region (density $< 10^3 \text{ cm}^{-3}$).
- ▶ An H_2 region in which starlight penetrates (density $\approx 10^3\text{--}10^4 \text{ cm}^{-3}$).
- ▶ A dense H_2 region opaque to starlight (density $\approx 10^4\text{--}10^7 \text{ cm}^{-3}$).

Gas-phase processes

For the formation of all species other than H_2 , we will consider only two-body gas-phase processes that can occur spontaneously in a very low-temperature medium. There are four main reasons for this approach. First, the rate constants for all processes to be utilized are obtainable either from direct laboratory investigation or feasible theoretical calculation. Secondly, the rates of the reactions are usually rapid compared with surface processes. It appears likely that, while material may both accrete on and evaporate from grains, it will be processed by gas-phase reactions. Thus, it is unlikely that any species formed on grains (other than H_2) can persist without change in the gas. Thirdly, the composition and surface character of the grains is unknown. Surface reactions at low grain temperatures on an unknown surface pose an unsolved mystery. Finally, because gas-phase reactions occur rapidly, a model of interstellar chemistry involving surface reactions must also include vir-

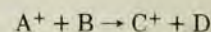
tually all of the gas-phase reactions.

It appears to us most profitable at this time, therefore, to develop a purely gas-phase model that can be compared with astronomical observations. (But note that this view is by no means universal.¹³) Discrepancies between model predictions and observations can then serve to indicate either surface processes or other processes not within the scope of the model. Examples of some other processes are: shock-wave induced reactions, high-temperature stellar atmosphere reactions followed by ejection of the products into clouds, and grain explosions. To determine numerical molecular abundances from a gas-phase model, it is convenient to assume that interstellar molecules are at steady-state—in other words, that their formation and depletion rates are the same. This assumption can be justified by demonstrating that the average time necessary to reach a steady-state condition is much smaller than the cloud lifetime.⁹

What gas-phase reactions are possible in a low-density medium whose temperature is at or below 100 K? The low density restricts possible reactions to binary collisions involving ground electronic-vibrational state species since, in general, the time between reactive collisions is so long as to permit most ordinarily forbidden radiative-emission processes to occur. The low temperature provides even more restrictive conditions. Reactions must be exothermic. The rate constant for elementary bimolecular chemical reaction is often fit to the simple Arrhenius formula

$$k = Ae^{-E_a/k_B T} \quad (\text{cm}^3/\text{sec}) \quad (1)$$

where A is the pre-exponential factor (which may contain a slight dependence on temperature), k_B is the Boltzmann constant, and E_a , the so-called "activation energy," is the minimum energy barrier that must be overcome to form products. The rate constant k , a macroscopic quantity, can be related to the reaction cross section σ by the relation $k = \langle \sigma v \rangle$, where v represents velocity and the average is taken over a thermal distribution. Most reactions between neutral species, even if exothermic, require an activation energy very much greater than $k_B T$ in the interstellar medium; thus $k(T)$ approaches zero. Exceptions are reactions between atoms and reactive molecules.⁸ Exothermic ion-molecule reactions of the type



hardly ever require activation energy and, consequently, dominate interstellar chemistry. An abundance of experimental evidence suggests that these reactions possess rate constants often *totally* independent of temperature; near the value predicted by the Langevin relation¹⁴

$$k = \langle \sigma v \rangle = 2\pi e(\alpha/\mu)^{1/2}$$

$$\approx 1-2 \times 10^{-9} \text{ cm}^3/\text{sec} \quad (2)$$

where e is the electronic charge, α the polarizability of the neutral reactant, and μ the reduced mass of the colliding species.

In the remainder of this article, we shall discuss specific gas-phase reactions that determine the chemistry of carbon, oxygen, hydrogen, and nitrogen in interstellar regions. Many important related topics are discussed in papers by William Watson and by Alexander Dalgarno, Michael Oppenheimer and John Black.¹⁵⁻¹⁸ Virtually all of the observed polyatomic molecules are to be found in dense H_2 regions opaque to light, and we will devote our attention to these regions. Unfortunately, space does not permit us to discuss the interesting interstellar chemistry of the lower density ("diffuse") H I and H_2 regions in this article.

Cosmic rays in the dense clouds

If molecular complexity is taken to be the criterion of interest, then the dense H_2 regions are of primary importance. The following discussion relies upon our own quantitative model,⁹ many aspects of which have been independently discussed by Watson.^{7,18}

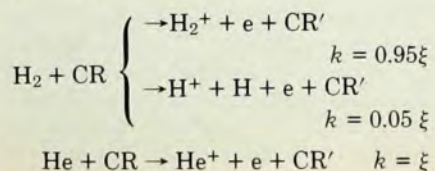
The penetration of interstellar ultraviolet radiation into dense H_2 regions is sufficiently low that photodissociation and photoionization need not be considered. Temperatures are typically low (6-50 K) except for small central cores associated with infrared objects where temperatures up to 150 K have been observed.⁴ The confirmed existence of the esoteric species HCO^+ , CCH , N_2H^+ , and HNC clearly indicates that these regions are *not* at chemical equilibrium. Thus, a flux of energy is required to maintain disequilibrium.

Throughout the galaxy there exists a roughly constant flux of high-energy cosmic rays with energies equal to or exceeding 100 MeV. These cosmic rays (chiefly protons) produce an ionization rate per interstellar atom or molecule, ξ , of around $10^{-17} \text{ sec}^{-1}$. This rate of ionization is minute compared with photoionization in diffuse clouds, but it takes on extreme importance in dense clouds. With perhaps the exception of the galactic center, dense clouds have insufficient matter to stop cosmic rays. Consequently, cosmic-ray-induced ionization occurs *throughout* the clouds. The quoted rate constant for ionization, $10^{-17} \text{ sec}^{-1}$, appears to be well established for high-energy ($\geq 100 \text{ MeV}$) cosmic rays. The flux of lower-energy cosmic rays is not well known. For dense clouds this uncertainty is not vitally important, because low-energy cosmic rays will not penetrate to the interior. Once a small amount of ionization is accomplished, a succession of ion-molecule reactions and

Table 2. Observed interstellar molecules		
Inorganic		Organic
	DIATOMIC	
H_2 hydrogen OH hydroxyl SiO silicon monoxide SiS silicon sulfide NS nitrogen sulfide SO sulfur monoxide		CH methylidyne CH^+ methylidyne ion CN cyanogen CO carbon monoxide CS carbon monosulfide
	TRIATOMIC	
H_2O water N_2H^+ H_2S hydrogen sulfide SO_2 sulfur dioxide		CCH ethynal HCN hydrogen cyanide HNC hydrogen isocyanide HCO^+ formyl ion HCO formyl OCS carbonyl sulfide
	4-ATOMIC	
NH_3 ammonia		H_2CO formaldehyde HNCO isocyanic acid H_2CS thioformaldehyde
	5-ATOMIC	
		H_2CNH methanimine H_2NCN cyanamide HCOOH formic acid HC_3N cyanoacetylene
	6-ATOMIC	
		CH_3OH methanol CH_3CN cyanomethane HCONH_2 formamide
	7-ATOMIC	
		CH_3NH_2 methylamine $\text{CH}_3\text{C}_2\text{H}$ methylacetylene HCOCH_3 acetaldehyde H_2CCHCN vinyl cyanide
	8-ATOMIC	
		HCOOCH_3 methyl formate
	9-ATOMIC	
		$(\text{CH}_3)_2\text{O}$ dimethyl ether $\text{C}_2\text{H}_5\text{OH}$ ethanol
The authors are indebted to Lewis Snyder (University of Illinois) for this list, which is complete as of 15 October, 1975.		

an ion-electron reaction occurs to produce a rich chemistry.

The chemistry of dense clouds is initiated by the slow cosmic-ray-induced ionization of the most abundant species— H_2 and He :



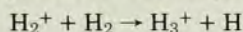
where CR and CR' are initial and final cosmic-ray energies. We need consider only these reactions as *primary* events, since all other species are far less abundant than H_2 and He (Table 1). What are the other species? For the purpose of modelling, we assume that initially the cosmic abundance of carbon is mainly in the form of carbon monoxide, that the oxygen abundance in excess of the CO density is in the form of O and O_2 , and that the nitrogen abundance is in the form of N and N_2 . No other elements will be

considered. The formation and prevalence of CO in moderate to dense clouds has been discussed by several authors.^{8,17} In addition, our assumption that virtually all carbon exists as CO is in agreement with observation. The high abundance of CO permits mapping of the universe in this species, as, for example, the map in CO of our galaxy shown in figure 3.

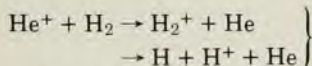
It should be emphasized that the initial conditions for this model of polyatomic synthesis need not resemble the steady-state conditions. We point out, however, that the steady-state conditions do in fact resemble the initial conditions as far as diatomic abundances are concerned.

Secondary reactions

Once H_2^+ is formed, it undergoes rapid secondary reaction with ubiquitous H_2 :

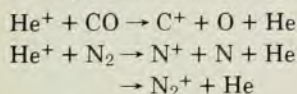


This reaction, the prototype for a large class of synthetic ion-molecule reactions, has been well studied and occurs at the Langevin rate. The atomic He^+ , on the other hand, reacts extremely slowly¹⁹ with H_2 :

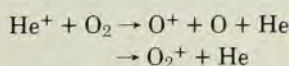


$$k(300\text{ K}) = 1.1 \times 10^{-13} \text{ cm}^3/\text{sec}$$

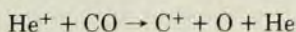
In view of the observation that this reaction increases in rate at higher He^+ energies, it may well be that the system possesses activation energy. In any event, the value of the rate constant at 300 K must be regarded as a severe upper limit at interstellar cloud temperatures. Ions such as He^+ that originate from abundant elements and that are not depleted by rapid reaction with molecular hydrogen have relatively high stationary abundances. The reactions of He^+ with diatomic species other than H_2 occur at or near the Langevin rate and are of considerable importance. These reactions:



and

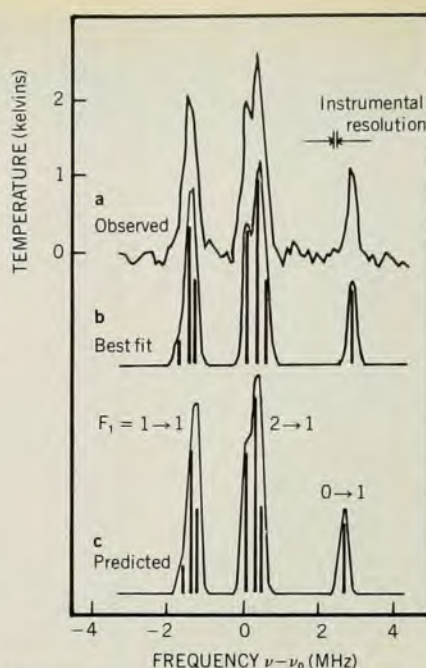


serve to provide efficient mechanisms for the production of C^+ , N^+ and O^+ . The reaction



is the most likely one to be responsible for the large number of organic (carbon containing) molecules listed in Table 2. Because C^+ does not react rapidly with either H_2 or CO, it is relatively stable in dense clouds. We will discuss reactions involving this ion below.

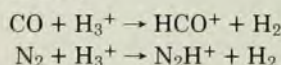
The immediate reactions of H_3^+ with neutral components of the clouds are also of extreme interest. Since H_3^+ does not



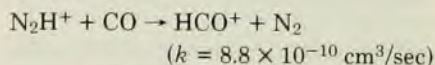
Spectroscopic constant	Best fit (MHz)	Theoretical (MHz)
$2(B_0 - 2D_0)$	93173.392(31)	92200(1800)
eq Q_{N_0}	-5.666(12)	-5.3(5)
eq Q_{N_1}	-1.426(21)	-1.2(5)
C_{N_0}	0.0147(23)	0.012

Rotational spectrum of the molecular ion HN_2^+ . Curve a shows the emission observed by Patrick Thaddeus and B. E. Turner in the source OMC-2. Curve b is this part of the spectrum calculated with constants chosen to give the best fit to the observed spectrum. Curve c is the same spectrum calculated with *ab initio* values of all molecular constants by Thaddeus, S. Green and J. A. Montgomery Jr. The table compares the "best fit" and *ab initio* spectroscopic constants $2B_0 - 4D_0$, the rotational transition frequency, eq Q_{N_0} and eq Q_{N_1} , the quadrupole couplings of outer and inner nitrogen, respectively, and C_{N_0} , the spin rotation of outer nitrogen. Figure 2

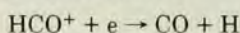
react with H_2 , it too is relatively abundant. H_3^+ does react with the species CO, N_2 , O and N. The reactions with CO and N_2 are well studied and proceed at the Langevin rate:



The species N_2H^+ is depleted principally via reaction with CO to produce more HCO^+ :²⁰



The species HCO^+ is one of the most stable molecular ions; it is depleted *only* by reaction with electrons



(The electron density is equal to the total positive-ion density.) Rate constants for polyatomic ion-electron dissociative recombination reactions are quite high— k up to about $10^{-6} \text{ cm}^3/\text{sec}$ —but the low density of electrons makes this mode of

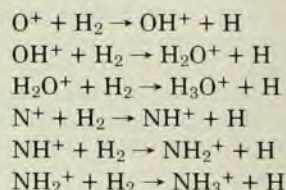
depletion usually slower than reaction with an abundant neutral such as CO. Thus, the ion-molecule scheme predicts that even if the densities of CO and N_2 are roughly equal, the abundance of HCO^+ should considerably exceed that of N_2H^+ .⁹ The radio observation of both HCO^+ and N_2H^+ at abundances in good agreement with those predicted by ion-molecule reaction schemes is a direct demonstration of the importance of such schemes to the chemistry of the interstellar medium.

Six reaction types

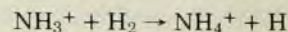
Returning to the synthesis of neutral, polyatomic species that comprise the vast majority of the observed species, we note that it is important to determine whether or not gas-phase reactions can account for their abundances. We shall focus, at first, on reactions that synthesize these species, and then discuss depletion reactions. Apparently a very large number of exothermic ion-molecule reactions and other reactions without activation energy must be considered; of particular importance are the six general types of reactions numbered 1-6 in the following discussion.

Type 1 $A + H_2 \rightarrow AH^+ + H$

where A^+ is an arbitrary ion. If this reaction proceeds with a rate constant near $10^{-9} \text{ cm}^3/\text{sec}$, then A^+ is efficiently converted to AH^+ in 10^4 sec . The ion AH^+ can continue to add additional hydrogen atoms by further reaction with H_2 . For example, O^+ and N^+ ions will be efficiently converted to polyatomic ions by the rapid, well-studied reactions



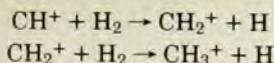
The reaction



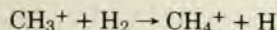
is exothermic but does not occur at the usual Langevin rate. In fact, F. C. Fehsenfeld and his colleagues²¹ have recently found that at temperatures in the range 300–800 K, the rate constant can be fit to equation 1 with parameters $A = 1.7 \times 10^{-11} \text{ cm}^3/\text{sec}$ and $E_a = 0.09 \text{ eV}$. This activation energy is much smaller than what is observed for the normal neutral-neutral reaction. However, extrapolated to 100 K, these parameters yield $k(100 \text{ K}) = 5 \times 10^{-16} \text{ cm}^3/\text{sec}$, a value small enough to limit the importance of this reaction sharply even though H_2 is so abundant. It is unclear whether such an extrapolation is reasonable, and additional, low-temperature data are needed.

Unlike O^+ and N^+ , the C^+ ion does not react exothermically with H_2 to form CH^+ . Since C^+ does not react with CO or N_2 either, it is expected to be relatively

abundant. If CH^+ is formed by a different process, it can be rapidly converted to CH_3^+ by the reactions



The reaction

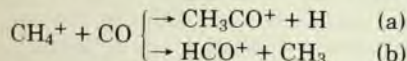


is however endothermic and therefore cannot occur.

Other reactions of type 1, not mentioned here, are contained in our model.⁹ The large abundance of H_2 makes it essential to know the rate constants of exothermic ion- H_2 reactions for all ions that can be produced under interstellar conditions.

Type 2 $\text{AH}^+ + \text{CO} \rightarrow \text{ACO}^+ + \text{H}$

Type 1 reactions serve to "hydrogenate" ions; that is, they increase the number of hydrogen atoms surrounding a heavy atom nucleus. Type 2 is an example of a reaction that increases the number of heavy atoms in a molecular ion. Because CO, although a prominent species, is more than three orders of magnitude less abundant than H_2 , reactions of type 2 are most important for ions that do not react rapidly with molecular hydrogen. H. I. Schiff and D. K. Bohme of York University have recently studied the reaction

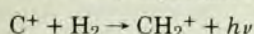


and found k_a/k_b to be not less than 3/7. These authors have promised to study the analogous $\text{CH}_3^+ + \text{CO}$ system, which may be more interesting astrophysically. The importance of type 2 reactions is difficult to gauge at this juncture. Experimental information for almost all systems of interest is lacking and is needed to determine whether CO can "insert" itself into a molecular ion (route a) or whether simple proton transfer (route b) is the only pathway.

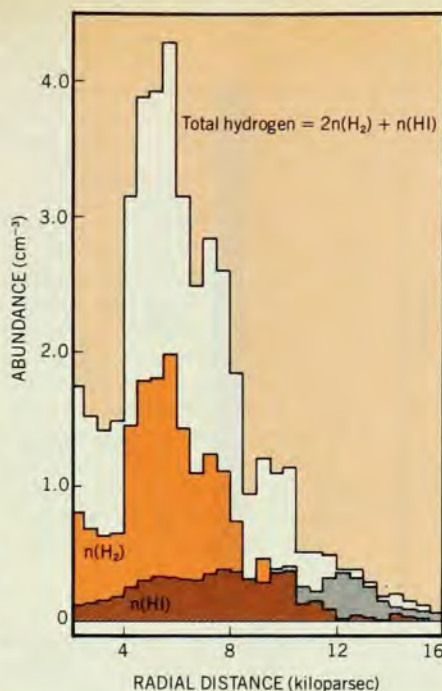
Type 3 $\text{A}^+ + \text{H}_2 \rightarrow \text{AH}_2^+ + h\nu$

where A^+ is an arbitrary ion that does not undergo a rapid type 1 reaction with H_2 . Reactions of type 3 are polyatomic analogs of the $\text{C}^+ + \text{H}$ radiative association shown in figure 4.

Because radiative association is such an inefficient process, it is necessary for H_2 to be one of the collision partners if the reaction rate is to be sufficiently rapid to be important. The important reaction

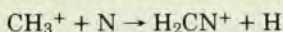


was suggested by Black and Dalgarno.¹⁶ They also discussed its importance for the formation of CH in diffuse clouds. Since C^+ is relatively abundant in dense clouds as well as diffuse clouds, this reaction is also important to dense-cloud chemistry. In dense clouds, it is a first step towards "carbon fixation" because CH_2^+ , once formed, reacts with H_2 to form CH_3^+ and



Radial distribution of interstellar gas, from M. A. Gordon and W. B. Burton of NRAO, Green Bank, W. Va. Observations of radio emission from CO enable a derivation to be made of the large-scale arrangement of cold compressed gas in the galaxy, even in distant regions inaccessible to optical observation. The abundance of H_2 (shown in color) is obtained with the assumption $n[\text{H}_2]/n[\text{CO}] = 1.7 \times 10^4$. Figure 3

H , and CH_3^+ can then undergo a variety of rapid ion-molecule reactions such as



A satisfactorily complete theoretical estimation of the $\text{C}^+ + \text{H}_2$ radiative association rate constant is extremely difficult. The CH_2^+ ion has two low-lying excited states, one of which is bound with respect to $\text{C}^+ + \text{H}_2$. It is necessary to have adequate knowledge of the potential surfaces of the ground state of CH_2^+ and both excited states, all of which correlate with ground state $\text{C}^+ + \text{H}_2$. It is also necessary to know the oscillator strength for transitions from the continuum of the bound excited state to discrete levels of the ground state. To utilize a semiclassical treatment, one must perform classical trajectory calculations. While allowing for curve crossing, which can occur in multi-surface problems, one must integrate the probability of spontaneous emission to the ground state along an excited-state trajectory and then average this integration over a large number of trajectories. The $\text{C}^+ + \text{H}_2$ problem is of sufficient importance to motivate our current calculation, which is being undertaken along these lines.

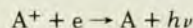
For larger polyatomic systems, Herbst²² has considered a statistical treatment for estimation of radiative association rate constants. In this treatment, the $(\text{AH}_2^+)^*$ collision complex formed in the collision of A^+ with H_2

transfers energy randomly among many vibrational modes. Spontaneous emission to stable (discrete) vibrational levels of the ground electronic state can occur from the "quasi-continuum" above the ground or low-lying excited state. The larger the $(\text{AH}_2^+)^*$ complex, and the more vibrational modes it possesses, the longer it "lives" before dissociating back into $\text{A}^+ + \text{H}_2$, and the larger the probability of radiative association. One system considered by Herbst²² was the reaction

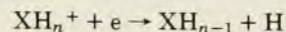


for which a rate constant of $k \leq 2 \times 10^{-17} \text{ cm}^3/\text{sec}$ was estimated at 50 K. This reaction may be of importance in the synthesis of formaldehyde (see below). However, there is some evidence that the $\text{HCO}^+ + \text{H}_2$ system possesses an unexpected activation energy barrier.²³

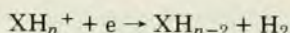
Type 4 $\text{A}^+ + e \rightarrow \text{neutral products}$ where A^+ is an arbitrary molecular ion. Reactions of the types 1, 2 and 3 synthesize larger molecular ions from smaller species. Type 4 reactions, labelled "recombination" reactions, serve to convert polyatomic ions into polyatomic neutrals. For molecular ions that do not react rapidly with the dominant neutral species (H_2 , CO, N_2), recombination reactions provide the major depletion route. It is well known that dissociative recombination to form smaller neutral species is much more rapid than radiative recombination



to form the parent neutral molecule. Typical, laboratory-determined, rate constants for the dissociative process are 10^{-6} – $10^{-7} \text{ cm}^3/\text{sec}$ for polyatomic ions and have a slight inverse dependence on temperature, whereas radiative recombination occurs three to four orders of magnitude slower. Atomic ion-electron reactions fall into the latter category and, consequently, ions such as C^+ are slowly depleted by reaction with electrons. Unfortunately, the branching ratios for the production of various sets of neutral species in dissociative recombination reactions are not known. For small polyatomic ions of the type XH_n^+ , where X is a single heavy atom, it is likely from statistical considerations that

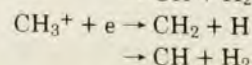
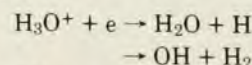


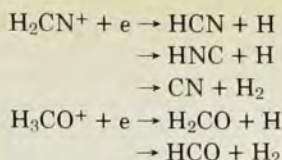
or



is favored over more complete (but still exothermic) fragmentation of the molecule. For ions with several heavy atoms, it is unclear what the distribution of fragments will be.

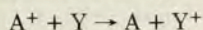
Some important recombination reactions are





Theoretical and laboratory studies to determine branching ratios are urgently needed.

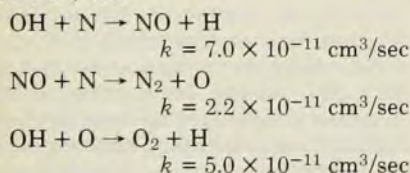
Neutral species can also be formed from polyatomic ions via simple charge-exchange processes of the type



where Y represents an easily ionized and possible abundant atom such as Si, Mg, or Fe.²⁴ Once neutrals are formed, they are depleted via chemical reaction in times long or short depending on their reactivity. Some especially reactive neutral species (for example, OH) are depleted principally via reaction with abundant neutral atoms. This process, which produces a wider variety of neutral species, will now be considered.

Type 5 $\text{A} + \text{B} \rightarrow \text{C} + \text{D}$

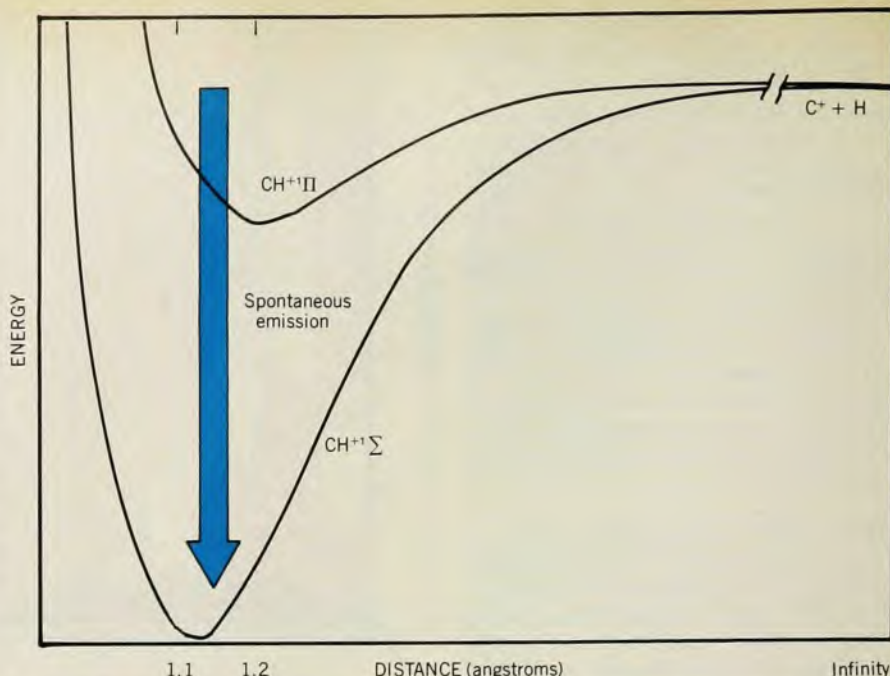
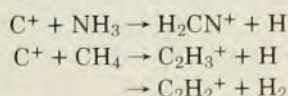
Reactions between neutral species need not usually be included because activation energy barriers are sufficiently large compared with $k_B T$ that rate constants are negligible. However, there are exceptions, principally reactions between atoms and reactive molecules. Examples of some important interstellar reactions and their laboratory-determined rate constants (roughly temperature independent) are:²⁵



These reactions serve to deplete species such as OH and NO within very short periods of time (say, 30 years). However, most neutrals are not depleted by reactions with other neutrals, but by ion-molecule reactions. The principal ions in a dense cloud are H^+ , C^+ , HCO^+ , H_3^+ , N_2H^+ , He^+ and H_3O^+ . Reactions with C^+ are especially noteworthy because they may produce ions with one more heavy atom than the reacting neutral:

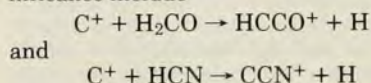
Type 6 $\text{C}^+ + \text{AH} \rightarrow \text{AC}^+ + \text{H}$

These reactions, in which AH is an arbitrary molecule with at least one hydrogen atom, are often exothermic. The AC^+ species produced can then undergo reactions of types 1 through 4 to produce new and larger neutral species with more heavy atoms than AH. Some examples of laboratory reactions as studied by Schiff, Bohme and their colleagues²⁶ are of this type



Radiative association in CH^+ . For radiative association to occur during a collision of $\text{C}^+(^2\text{P})$ and $\text{H}(^2\text{S})$, spontaneous emission must occur from the continuum of the $\text{A}^1\Pi$ state to discrete vibrational levels of the ground $\text{X}^1\Sigma^+$ state; it occurs approximately once in 10^8 collisions. Figure 4

Much work remains to be done, especially on reactions of C^+ with many of the smaller species known to be present in dense clouds. Reactions of possible significance include



How good is the model?

Our present model for the specific synthesis of interstellar molecules in dense H_2 clouds may be summarized as cosmic-ray-induced ionization of H_2 and He followed by a wide variety of ion-molecule reactions. Neutral molecular species are in general formed by dissociative recombination reactions between ions and electrons. Neutral species are then depleted either by reaction with neutral atoms or molecular and atomic ions. These reactions are entirely gas-phase two-body processes.

Our detailed model considers around 100 reactions, principally of types 1 through 6, involving 37 species of up to five constituent atoms each. Steady-state abundances are presented as a function of H_2 density for H_2 densities between 10^4 and 10^6 cm^{-3} . Quantitative agreement between theory and observation is reasonable, considering the vagaries involved in both approaches. The calculated abundances of certain species, however, do depend to some extent on the ratio of the oxygen to carbon cosmic abundance values that we use. This dependence is most marked for ionic rather than neutral species. If, as shown in Table 1, O/C is about 2, then the overwhelmingly dominant interstellar ion is HCO^+ ; on the other hand, if O/C is closer

to unity, C^+ becomes the dominant ion. The apparent sensitivity of these results to the O/C abundance ratio may be an artifact of an incomplete analysis. It is our opinion, however, that the ionic constituents of dense clouds do in fact reflect the heavy-atom cosmic abundance ratios present in each cloud. If this interpretation is correct, one inference can be drawn immediately: Because production of organic species larger than those considered in the model depends to a large extent on reactions of type 6 between C^+ and neutral species, an O/C abundance ratio of about 2 is probably incompatible with gas-phase molecular syntheses of larger (5–9 atomic) organic compounds. This conclusion is hardly striking or novel—in a strongly oxygen-rich environment, oxidation will occur by one means or another (gas-phase or perhaps even grain-catalyzed) to retard organic development. It is therefore our tentative conclusion that the O/C abundance ratio pertaining to the gas phase of dense clouds where organic molecules are observed must be smaller than 2.

Despite this uncertainty, it is important to ask whether or not gas-phase reactions can account for the richness and complexity of the observed chemistry in dense clouds. The extension of gas-phase modelling to species larger than 4 or 5 atoms involves a vast number of reactions. In addition to this obvious difficulty, we are confronted with two further obstacles:

► lack of rate-constant data.

For many ion-molecule reactions of possible importance to interstellar chemistry, rate constants have yet to be determined in the laboratory. It is tempting to assign

Langevin rate constants to these systems. Even if this is done, however, the problem of unknown branching ratios becomes more and more severe as larger molecules react.

► lack of thermodynamic data.

For many polyatomic ions of interest, thermodynamic data are sketchy or non-existent. Thus, it is not even possible to determine the exo- or endothermicity of many reactions of possible importance.

In the near future, these two obstacles should disappear, allowing more reliable gas-phase modelling of polyatomic dense-cloud chemistry. This development will open one of the most interesting problems of interstellar chemistry—the question of how large organic molecules can form in the harsh environment of interstellar space. Molecular clouds are among the most massive objects in the galaxy. Their complex chemistry must be unraveled if we are to comprehend the process of molecular evolution throughout the universe.

The work we have discussed here is directed entirely to the molecular chemistry of the interstellar medium. As such, it ignores in large measure the interplay of physical conditions with the spectral observation of molecular species. At this stage, simple models capable of producing

general agreement with observation are sought. Without undue optimism, it appears to us that, when obvious present deficiencies of gas-phase models become removed, it should be possible to use the chemistry of the interstellar medium as a probe for measuring the heterogeneity of physical conditions therein.

We have limited this discussion to the chemistry of a static, relatively homogeneous region. The question of the chemical evolution through the condensation of, say, the solar nebula—a question likely to be coupled to the origin of life—is certainly of great interest. The progress of the last few years in observation and theory of the molecular composition of the interstellar medium provides much hope for further understanding in this decade.

* * *

This article is an adaptation, by the authors, of their talk delivered at the Ninth International Conference on the Physics of Electronic and Atomic Collisions, held at Seattle, Washington, 24–30 July 1975. The text of the original paper is published in The Physics of Electronic and Atomic Collisions, J. S. Risley and R. Geballe, eds., University of Washington Press 1976 (a partial "Proceedings" of the Conference), and this version appears here by permission of the editors of that publication.

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