MOLECULAR CLOUDS, STAR FORMATION AND HII REGIONS

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CHEMISTRY OF MOLECULAR CLOUDS

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Abstract

A discussion is presented of the chemistry of quiescent molecular clouds, and the effects of the presence of polycyclic aromatic hydrocarbon molecules and of cosmic-ray induced ultraviolet photons are examined. A comparison is made with the chemistry occurring in molecular clouds that are subjected to shocks and the differences between dissociative and non-dissociative shocks are described. The changes in composition caused by intense cosmic ray fluxes or intense ultraviolet radiation fields are explored.

1. Introduction

Molecular clouds in the interstellar medium are characterized as diffuse, translucent or dense, depending on the column density of material contained in the clouds. Diffuse clouds correspond to visual extinctions A_V less than about one magnitude, equivalent to a column density N_H of hydrogen nuclei less than 1.9×10^{21} cm^{-2}. Translucent clouds are more extended with visual extinctions between one and five magnitudes. Dense clouds have visual extinctions greater than five magnitudes. Dense clouds include clouds in which active star formation is in progress and dark clouds which appear to be quiescent.

Diffuse and translucent molecular clouds only partly obscure the light from the stars that lie behind them and they have been studied mostly through observations of the absorption lines in the ultraviolet, visible and infrared spectrum to which they give rise. Some molecules in diffuse, and more so in translucent clouds, have been detected also through the appearance of emission lines in the millimetre region. The penetration of the interstellar radiation field diminishes exponentially with A_V and molecules in dense molecular clouds are detectable through their emission and absorption lines in the millimetre and radio regions.

The densities of molecular clouds range from about 10^2 cm^{-3} characteristic of diffuse and translucent clouds to 10^3 cm^{-3} or 10^4 cm^{-3} characteristic of dense clouds though clumps of much higher density also occur. The temperatures range from about 70K or more in diffuse clouds to 10K in dark clouds. Temperatures may be higher in localized regions which have been disturbed by processes associated with star formation and stellar evolution.

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A diverse array of molecules has been discovered in dense clouds. The list contains over seventy-five distinct species and includes many complex organic molecules and several molecular ions. Interstellar molecules have been detected containing the elements hydrogen, carbon, oxygen, nitrogen, sulphur, silicon, chlorine and phosphorous. In dense clouds where the complex molecules are found, carbon monoxide has an abundance relative to hydrogen of about 10^{-4} and the other molecules have fractional abundances between 10^{-7} and 10^{-10} (cf. Irving, Goldsmith and Hjalmarson 1987). In diffuse and translucent clouds, only diatomic molecules have been observed, though C_3H_2 has been detected in an apparently diffuse region towards Cas A. There is also indirect evidence for the presence of very large molecules containing more than twenty carbon atoms in the diffuse interstellar medium and in diffuse molecular clouds.

The chemical composition in molecular clouds and its response to intense radiation fields, ehhanced ionization sources, dissociative and non-dissociative shocks and to the interactions of outflowing material from protostellar objects, evolving stars, novae and supernovae is a potentially significant source of information about the structure and evolution of interstellar clouds and of the mechanism by which stars are formed in the Milky Way galaxy and external galaxies. The chemical composition affects the cloud evolution through its influence on the thermal and ionization balance and may yet serve as a chemical clock for determining the age of clouds.

2. Chemistry

The chemistry of molecular clouds is broadly the chemistry of a gas of molecular and atomic hydrogen and atomic helium with a small admixture of heavy elements. The gas contains solid refractory dust grains. The grains play a crucial role in excluding the photons of the interstellar radiation field from the interiors of large clouds and thereby shielding the molecules from the destructive effects of photodissociation. They are important also as sites for the formation of molecular hydrogen and possibly of other molecules and as sinks for the removal of heavy atoms and molecules from the gas phase.

In diffuse and translucent clouds and in the outer envelopes of dense clouds, photodissociation and photoionization are significant events in the chemistry. For clouds near to external intense sources of ultraviolet radiation, processes initiated by the absorption of the photons exert a major influence on the chemistry for distances into the clouds up to and beyond $A_V = 5$. Those molecular envelopes subjected to intense ultraviolet radiation have been called photodissociation regions (Tielens and Hollenbach 1985) or photochemical regions (van Dishoeck 1988).

In addition to the interstellar radiation field, the clouds are bombarded by cosmic rays. Ionization caused by the cosmic rays leads to the formation of molecular ions whose presence in the interiors of interstellar clouds has been established

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observationally. Because many neutral particle reactions have activation barriers and are slow at the temperatures prevailing in molecular clouds, the chemistry is mainly an ion-molecule chemistry driven by the interstellar radiation field in the outer envelopes and by cosmic rays in the interiors. Most ion-molecule reactions remain rapid at low temperatures and for heteronuclear molecules may increase in efficiency.

In the envelope, carbon is ionized by interstellar photons and the carbon chemistry is initiated by the radiative association

$$C^+ + H_2 \rightarrow CH_2^+ + h\nu \ . \qquad (1)$$

In the interior, reaction(1) occurs but the major source of C^+ is the charge transfer reaction

$$He^+ + CO \rightarrow C^+ + O + He \ , \qquad (2)$$

the He^+ being a product of cosmic ray ionization. Following (1), the abstraction reaction

$$CH_2^+ + H_2 \rightarrow CH_3^+ + H \qquad (3)$$

occurs. The molecular ion CH_3^+ may be removed by dissociative recombination

$$CH_3^+ + e \rightarrow CH_2 + H \qquad (4a)$$

$$\rightarrow CH + H_2 \qquad (4b)$$

but in dense clouds where the electron density is low, radiative association with H_2 to form CH_5^+,

$$CH_3^+ + H_2 \rightarrow CH_5^+ + h\nu \ , \qquad (5)$$

may occur more rapidly. In diffuse regions, CH_2 formed in process (4a) is photodissociated to yield CH,

$$CH_2 + h\nu \rightarrow CH + H \ . \qquad (6)$$

Methane can be formed from CH_5^+ by reaction with CO,

$$CH_5^+ + CO \rightarrow CH_4 + HCO^+ \ . \qquad (7)$$

Complex hydrocarbons can then be built by insertion reactions. An example is the reaction

$$C^+ + CH_4 \rightarrow C_2H_3^+ + H \ . \qquad (8)$$

Dissociative recombination,

$$C_2H_3^+ + e \rightarrow C_2H_2 + H \ , \qquad (9)$$

then leads to acetylene. Condensation reactions such as

$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2 \qquad (10)$$

are also effective.

Reactions of the hydrocarbon ions with neutral heavy atoms lead to the formation of molecules incorporating oxygen, nitrogen, sulphur and other elements. Thus

$$C_2H_4^+ + O \rightarrow C_2H_3O^+ + H \quad (11)$$

$$C_2H_3O^+ + e \rightarrow CH_2CO + H \quad (12)$$

is a source of ketene and

$$C_2H_4^+ + N \rightarrow C_2H_3N^+ + H \quad (13)$$

$$C_2H_3N^+ + e \rightarrow CH_2CN + H \quad (14)$$

is a source of the cyanomethyl radical CH_2CN.

Cosmic ray ionization of H_2 to produce H_2^+ leads to H_3^+,

$$H_2^+ + H_2 \rightarrow H_3^+ + H \quad . \quad (15)$$

The molecular ion H_3^+ undergoes proton transfer

$$H_3^+ + X \rightarrow HX^+ + H_2 \quad (16)$$

with many of the neutral systems X. The ion HX^+ then initiates a sequence of abstraction reactions. Thus

$$H_3^+ + C \rightarrow CH^+ + H_2 \quad (17)$$

leads to CH_3^+ and

$$H_3^+ + O \rightarrow OH^+ + H_2 \quad (18)$$

leads to H_3O^+. Dissociative recombination of H_3O^+ produces H_2O and possibly OH. In diffuse and translucent clouds the oxygen sequence can also be by H^+ ions, produced by cosmic ray ionization of H, which undergo charge transfer

$$H^+ + O \rightarrow H + O^+ \quad (19)$$

followed by

$$O^+ + H_2 \rightarrow OH^+ + H \quad . \quad (20)$$

In both diffuse and dense clouds the production of OH is proportional to the cosmic ray ionization rate and the abundance of OH is a measure of the flux of cosmic rays penetrating the clouds.

Radiative association reactions are effective in building large molecules and in mixing the different element chemistries. Methanol can be formed by

$$CH_3^+ + H_2O \rightarrow CH_3OH_2^+ + h\nu \quad (19)$$

$$CH_3OH_2^+ + e \rightarrow CH_3OH + H \quad (20)$$

and ethanol by

$$H_3O^+ + C_2H_4 \rightarrow CH_3CH_2OH_2^+ + h\nu \quad (21)$$

$$CH_3CH_2OH_2^+ + e \rightarrow CH_3CH_2OH + H \quad . \quad (22)$$

Comprehensive accounts of the chemistry of complex molecules and the results of detailed calculations of the molecular abundances have been presented by Graedel and Langer (1989) and Herbst and Leung (1989). Their models do not take full account of the effects of the ultraviolet photons that are generated internally by the cosmic rays (Prasad and Tarafdar 1983). The secondary electrons accompanying ionization by cosmic rays excite molecular hydrogen and the excited states decay by spontaneous emission in the ultraviolet, producing photons that are energetically capable of photodissociating many and photoionizing some of the interstellar molecules (Sternberg, Dalgarno and Lepp 1987). The destructive effects of the cosmic ray-induced photons amplify along a chemical chain as molecules are built by the addition of carbon atoms. The effects are mitigated by the photodissociation of CO

$$CO + h\nu \rightarrow C + O \quad . \tag{23}$$

It happens that many of the emission lines of H_2 overlap the absorption lines of CO that lead to dissociation of CO (Gredel, Lepp and Dalgarno 1987).

Photodissociation of CO by the cosmic ray-induced photons is a major source of neutral carbon atoms which counteracts the tendency of carbon to accumulate into CO and thereby limit the abundances of the complex hydrocarbons. Thus in model calculations of Gredel et al. (1989), the inclusion of the photodissociation of CO increases the steady-state C/CO ratio from 5×10^{-5} to 6×10^{-3} and the C_3H_2/H_2 ratio from 2×10^{-12} to 2×10^{-11}.

The steady-state ratios are however considerably smaller than values found in many observations. The C/CO ratio is as large as 0.1 or 0.2 in many clouds (cf. Keene et al. 1985, Genzel et al. 1988) and the C_3H_2/H_2 abundance ratio is typically in the range $10^{-9.5}$–$10^{-8.4}$ (Cox, Walmsley and Gusten 1989). Steady-state models (cf. Graedel and Langer 1989, Herbst and Leung 1989) are fairly successful in predicting the abundances of the smaller molecules (though serious discrepancies persist between the model abundances and observations of diffuse and translucent clouds (cf. van Dishoeck and Black 1986, 1988, 1989; Viala 1986, Viala, Roueff and Abgrall 1988, Nercessian, Benayou and Viala, 1988) but fail for the complex species despite the flexibility offered by the absence of laboratory data on many of the reactions involved in the chemical models.

One explanation of the high C/CO ratio and the high abundances of complex molecules is a carbon abundance that is in excess of the oxygen abundance so that an ample supply of carbon remains after the formation of carbon monoxide is complete (cf. Graedel and Langer 1989). Mechanisms by which gaseous carbon could be more abundant than gaseous oxygen in the cloud interiors have been discussed by Blake et al. (1989). There may be difficulty in reproducing the abundances of the alcohols though cosmic ray-induced photodissociation of CO (and of O_2 and H_2O) will be a large source of oxygen atoms.

The chemistry will be modified if a substantial population of large molecules or very small grains exists in dense clouds. There is considerable spectroscopic evidence from observations of infrared sources that such systems form a major component of the diffuse interstellar medium with an abundance relative to hydrogen of the order of 10^{-7} (cf. Puget and Leger 1989). The explicit identification of the large molecules as polycyclic aromatic hydrocarbons, containing in excess of twenty carbon atoms, has been advanced.

An immediate consequence of the presence of large molecules LM in dense clouds is the neutralization of atomic ions that do not react with H_2 by charge transfer

$$C^+ + LM \rightarrow C + LM^- \qquad (24)$$

and mutual neutralization

$$C^+ + LM^- \rightarrow C + LM \quad . \qquad (25)$$

The chemistry is changed qualitatively as mutual neutralization replaces dissociative recombination (Lepp and Dalgarno 1988).

Models of diffuse molecular clouds (van Dishoeck and Black 1986) consistently underestimate the C^+/C ratio (Dalgarno 1988). Agreement can be obtained by postulating the presence of a component of large molecules with an abundance ratio to hydrogen of 1×10^{-7} for the cloud towards ζ Persei and of 6×10^{-7} for the cloud towards ζ Ophiuchi (Lepp et al. 1988).

Of potentially greater significance to interstellar chemistry is the contribution from chemical reactions of oxygen, carbon, nitrogen, silicon and sulphur with the large molecules. Some theoretical discussion of their chemistry has been given by Omont (1986), Duley and Williams (1986), Lepp et al. (1988) and Brown et al. (1989) and some laboratory measurements on the reactions of Si^+ with the polycyclic aromatic hydrocarbon, napthalene, have been reported (Bohme, Wlodek and Wincel 1989). Also of importance may be the interaction of cosmic rays with large molecules. Experimental studies have shown that the ions CH_3^+, $C_2H_2^+$ and $C_3H_3^+$ are major products of the ionization of polycyclic aromatic hydrocarbons by impacts of 70eV electrons (Kingston et al. 1985).

The collision frequency of large molecules with each other at an abundance ratio of 10^{-7} is high so that they will tend to grow in size and decrease in density. The chemistry will be time-dependent.

Time-dependent chemistry has been invoked to explain both the high C/CO ratio and the high abundances of hydrocarbons. Because the time scale for the accumulation of C into CO is longer than that for the formation of complex molecules, a time-dependent evolution from an initial configuration in which the carbon exists as neutral atoms produces at times of the order of 10^5 years substantial amounts of complex molecules while retaining much of the carbon in the form of C. The C_3H_2/H_2 ratio reaches peak values of about 10^{-7} (cf. Herbst and Leung 1989, Gredel et al. 1989), larger indeed than the observed ratios.

Leaving aside the question of the plausibility of such an initial condition, during the evolution of a dense molecular cloud, atoms and molecules will be lost from the gas phase by freezing on to the surfaces of grains in a time scale of less than 10^6 years. Absorption features found in the spectra of embedded infrared objects show that mantles containing H_2O, CO and other species form on grain surfaces. There should exist regions within clouds that are devoid of molecules (Williams 1985) except H_2 and the molecular ions H_3^+, H_2D^+ and HeH^+. They have not been found and there must be mechanisms for returning the grain material to the gas phase.

Desorption from interstellar grains by cosmic ray impact has been explored by Leger, Jura and Omont (1985). The explosive release of molecules in grain-grain collisions has been considered by d'Hendecourt, Allamandola and Greenberg (1985), who have presented time-dependent models of the chemical composition of the gas phase and of the grain surfaces in an interstellar cloud. The models predict large abundances of water and ammonia but carbon atoms are removed rapidly and the C/CO ratio falls steeply after a time of 10^5 years. The models do not consider complex molecules but it is probable that they follow qualitatively the longtime behaviour of neutral atomic carbon.

Grain-grain collisions may be insufficent and the chemistry may be influenced by sporadic events like star formation and by interactions with material flowing out from stars and protostars. Molecular formation in circumstellar shells has received considerable theoretical attention (cf. Nejad and Millar 1987, Glassgold et al. 1987, Mamon, Glassgold and Huggins 1988) and molecular formation in winds from protostars has been discussed by Rawlings, Williams and Canto (1988) and Glassgold, Mamon and Huggins (1989), in nova outbursts by Rawlings (1988) and in supernovae by Lepp, Dalgarno and McCray (1988, 1989), Petuchowski et al. (1989) and Latter and Black (1989).

The high velocity outflows drive shocks into the interstellar gas and compress and heat it. In the warm gas, the chemistry is driven by exothermic and endothermic reactions with H_2 of the kind

$$X + H_2 \rightleftarrows XH + H$$

and the resulting composition depends on the temperature and the H/H_2 ratio. Shocked gas is an efficient source of CH^+,

$$C^+ + H_2 \rightarrow CH^+ + H \quad ,$$

which may help to explain observations of CH^+ in diffuse clouds (Elitzur and Watson 1980, Draine 1986, Pineau des Forets et al. 1986), and of sulphur-containing molecules (Hartquist, Oppenheimer and Dalgarno 1980, Pineau des Forets, Roueff and Flower 1986) and in some environments shocks may enhance the formation of complex molecules (Mitchell 1983).

If the shock velocity exceeds 40km s^{-1}, all the molecules are destroyed. The subsequent chemistry is modified by the precursor ultraviolet radiation emitted in the cooling recombining post-shock gas (Hollenbach and McKee 1989, Neufeld and Dalgarno 1989). The CO/H_2 ratio is high and detectable populations of molecular ions may be produced as the gas passes through its warm ionized state (Neufeld and Dalgarno 1989). Complex species are not formed in any abundance in the warm gas.

The outflowing gas may itself be an important source of gas phase molecules, and its interaction with the grains is likely to remove the grain mantles and deposit further molecules into the gas phase. Observations of ammonia (Walmsley et al. 1987), water (Hinkel et al. 1987, Plaubeck and Wright 1987, Jacq et al. 1988) and methanol (Wilson et al. 1989) in the Orion-KL region all suggest that the molecules were evaporated from dust mantles heated less than 10^4 years ago. The different chemical composition in the ridge, plateau and hot core regions of the Orion molecular cloud are indications of the influence of star-forming events on the grain and gas chemistries (Blake et al. 1989).

The observations appear to demand a combination of a chemistry like that of diffuse clouds which is dominated by photoabsorption and a chemistry like that of dense clouds which is dominated by cosmic ray ionization, as would occur in a cloud containing dense clumps of material embedded in a diffuse inter-clump medium. Such a model has been postulated by Genzel et al. (1988), who attribute the high abundances of C^+ and C in M82 to ultraviolet photons penetrating into a clumpy gas.

Material will be exchanged between the diffuse and dense regions. A study of the chemical consequences of such mixing has been carried out by Chieze and Pineau des Forets (1989). Possible sources of the mixing are turbulence (Boland and de Jong 1982) and shocks (Williams and Hartquist 1984). A detailed scenario has been presented for the molecular cloud Barnard 5 which was earlier regarded as quiescent, but is now recognized as an active site (Charnley et al. 1988, 1989). According to it, ionized hydrogen and helium in stellar winds mix with molecular material ablated from the clumps.

The chemistry of molecular clouds is the result of complex interactions of stars as they evolve with the material out of which stars are formed. It should be posible to develop theoretical models with sufficient precision that the chemical composition can serve as a diagnostic probe of the history of the events that have taken place in the evolution of molecular clouds.

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Discussion:

KHAN: If there is a large density contrast between the molecular cloud and the outside medium, say ρ_m/ρ_0, then the gas in the cloud experiences a shock with speed $V_0\sqrt{\rho_0/\rho_m}$, and this can be much smaller than Vo, the speed with which the cloud advances relative to the outside medium.

DALGARNO: The limiting shock velocity above which CO is dissociated is about 50 kms^{-1}.

WAMPLER: SN 1987A is incased in a rather dense, slow moving, progenitor wind. Can the CO molecules survive their encounter with this wind a few decades from now?

DALGARNO: See remark by Dr. Kahn.