

# Interstellar chemistry

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In the past half century, radioastronomy has changed our perception and understanding of the universe. In this issue of PNAS, the molecular chemistry directly observed within the galaxy is discussed. For the most part, the description of the molecular transformations requires specific kinetic schemes rather than chemical thermodynamics. Ionization of the very abundant molecular hydrogen and atomic helium followed by their secondary reactions is discussed. The rich variety of organic species observed is a challenge for complete understanding. The role and nature of reactions involving grain surfaces as well as new spectroscopic observations of interstellar and circumstellar regions are topics presented in this special feature.

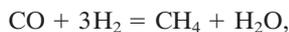
Interstellar chemistry began in the 1930s with the observation of molecular absorption spectra in distant stars within the galaxy. The species CH, CH<sup>+</sup>, and CN have electronic spectra in an accessible wavelength region where the earth's atmosphere is still transparent (1). These transitions in translucent clouds show a population distribution in rotational states, which was later understood to be determined by coupling of the polar species CH, CH<sup>+</sup>, and CN to the cosmic background radiation rather than by collisions (2). The character of these observable interstellar clouds are low-density and essentially atomic with a small diatomic molecular component. Our realization that the universe is highly molecular is quite recent (3). The discovery of microwave emission from the inversion transition of ammonia (4) located in the direction of the galactic center produced a fundamental change in the perception of the interstellar medium of the galaxy from a low-density, essentially atomic one to a highly heterogeneous one with great density variation. The discovery of molecular microwave emission was a surprise because everyone knew that to have thermal emission by heating the species above the temperature of the cosmic background radiation, the effective collision frequency must exceed the spontaneous emission rate, which for the ammonia inversion is 10<sup>-7</sup> sec<sup>-1</sup>. Assuming the typical collision rate constant of 10<sup>-10</sup> cm<sup>3</sup> requires a density of 10<sup>3</sup> cm<sup>-3</sup>, 10<sup>3</sup> greater than the average galactic density, to thermally pump the inversion transition of NH<sub>3</sub>. This discovery was exciting and led immediately to the understanding that high-density regions existed.

Radioastronomy was an ideal tool for detecting molecules. It is generally easier to see emission rather than absorption spectra. Furthermore, rotational transition frequencies can be estimated from molecular structure as well, of course, from laboratory measurement. Large high-density regions, giant molecular clouds, were soon found and in them a rich chemistry. The list of mo-

lecular species observed, interstellar and circumstellar, grew at a rate of four molecules per year, at which rate it is presently growing (3, 5). An excellent currently maintained web site is Molecules in Space ([www.ph1.uni-koeln.de/vorhersagen](http://www.ph1.uni-koeln.de/vorhersagen)). A listing with references to the initial observations is Interstellar & Circumstellar Molecules ([http://198.144.204.232/astrochymist/astrochymist\\_ism.html](http://198.144.204.232/astrochymist/astrochymist_ism.html)).

The nature of the selection of species is not transparent. While hydrogen (330,000) and helium (46,000) constitute over 99% of the universal material, the next abundance ordering is oxygen (230), carbon (100), nitrogen (30), and {Mg (11), Si (10), S (5), Fe (9)}. The molecular abundances do not follow the cosmic abundance of the elements. In particular, of the observed species with 6 or more atoms (presently 39 species), all contain carbon. Of the 4- and 5-atom species (34), only H<sub>3</sub>O<sup>+</sup>, NH<sub>3</sub>, and SiH<sub>4</sub> are nonorganic. Thus, the chemistry of positively identified polyatomic species observed in the gas phase is carbon chemistry. The explanation of this is interesting (6).

First, the chemistry of molecular clouds is kinetically rather than thermodynamically controlled. With cloud temperatures near 20 K, equilibrium calculations are quite simple. Two examples, of many, may be presented. The isomers HCN and HNC are observed in equal abundance in cold clouds. Their energy difference is 65.5 kJ·mol<sup>-1</sup>, thus at 20 K the predicted ratio is HCN/HNC = 10<sup>170</sup>. Perhaps even more dramatic is the hydrogenation of carbon monoxide, the second most abundant molecule, to methane and water,



where the ratio of [CH<sub>4</sub>][H<sub>2</sub>O]/[CO][H<sub>2</sub>]<sup>3</sup> predicted at equilibrium differs from interstellar observation by >500 orders of magnitude. [We may note that the hydrogenation steps to methane formation probably involve a sequence of hydrogenation steps. The first, CO + H<sub>2</sub> = H<sub>2</sub>CO, is 7 kJ·mol<sup>-1</sup> endothermic in the gas phase. Thus,

efficient conversion of CO to CH<sub>4</sub> is clearly easily inhibited at 20 K.] Therefore, a large body of interstellar chemistry is kinetically determined. In regions where high densities and high temperatures are integral to the evolution, such as stellar outflows, detailed kinetic schemes are frequently not required and the simpler equilibrium arguments may suffice (5).

The heterogeneity of interstellar and circumstellar regions gives rise to a variety of chemistries. It appears that the simplest regions are giant molecular clouds whose bulk is not penetrated by optical radiation from either the galactic radiation field or that from nearby stars. In these regions, temperatures are 10–20 K and the molecular processes, not being at thermodynamic equilibrium, require energy input to initiate. Because optical radiation does not penetrate, as may be readily seen in the photographs of a dark molecular cloud (see Molecular Cloud Barnard 68; <http://antwrp.gsfc.nasa.gov/apod/ap041219.html>). However, high-energy [100 MeV (1 eV = 1.602 × 10<sup>-19</sup> J)] cosmic rays penetrate and produce volume ionization (7, 8). The chemistry is initiated by the primary ionization of H<sub>2</sub> and He, which constitute >99% of the cosmic material in molecular clouds, producing primarily H<sub>2</sub><sup>+</sup> and He<sup>+</sup>. H<sub>2</sub><sup>+</sup> is very rapidly converted to H<sub>3</sub><sup>+</sup> by reaction with H<sub>2</sub>. Initially, the presence of nonpolar H<sub>3</sub><sup>+</sup> was surmised from observations of rotational transitions of the very abundant highly polar ion HCO<sup>+</sup> (3), produced by proton transfer from H<sub>3</sub><sup>+</sup> to CO. These exoergic ion-molecule reactions proceed, as expected, at collision frequency. The chemistry of He<sup>+</sup>, however, shows the need to know details. The electron transfer reaction He<sup>+</sup> + H<sub>2</sub> = {HeH<sup>+</sup> + H; He + H<sub>2</sub><sup>+</sup>; etc.}, resulting in the destruction of He<sup>+</sup>, is strongly inhibited, essentially not occurring at low collision energies (9, 10). Thus, He<sup>+</sup> is stable in the H<sub>2</sub> medium,

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reacting with CO at collision frequency to produce  $C^+ + O$ . The ionization of He is thus quantitatively transferred to  $C^+$  production, with the enhancement of the He/CO abundance ratio, of three orders of magnitude. The reactions of  $C^+$  then produce the rich organic chemistry observed. This ion-molecule kinetic scheme (6) has provided insights and interrelations for molecular abundances. The question of its completeness for a major portion of interstellar chemistry, that occurring in the optically dense molecular clouds, is discussed in several of the articles in this special feature.

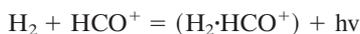
Obviously, it is far-fetched to assume a uniform chemistry within the highly heterogeneous universe. We may ask then within the galaxy how large a region may be regarded as homogeneous chemically. Insight into this question is provided by Snyder (3) using the increasing spatial resolution afforded by very long baseline interferometry. The question of the chemistries is broad. The role of the interstellar dust (11) in molecular growth is important. Because hydrogen is the dominant element, the recombination of H atoms to form  $H_2$  molecules will be the preponderant interstellar reaction. The question of grain surface synthesis of species that have strong binding to surfaces poses interesting observational questions. The desorption of species by cosmic ray heating is among the important questions of grain chemistry. These points are discussed by Herbst and Cuppen (11). The production of atomic hydrogen in dense molecular clouds is achieved primarily by cosmic ray ionization of  $H_2$ . The  $H_2^+$  reacts virtually immediately  $H_2^+ + H_2 = H_3^+ + H$ . Dissociative electron attachment to a protonated species,  $H_3^+$ , or its reaction product,  $HCO^+$ , yields atomic hydrogen. There appears to be good agreement between predicted and observed  $H_3^+$  abundance in dense molecular clouds (7). For every  $H_2$  ionization, 2H atoms are ultimately produced. Thus, the rate of production of H atoms is known. Therefore, determination of the H atom abundance in molecular clouds will provide an assessment of the H atom recombination velocity. Quite clearly, the high abundance of atomic hydrogen throughout the galaxy, and the transparency of the molecular clouds at 21 cm, requires careful correlation of the H atom abundance with CO the measure of molecular  $H_2$ .

The nonuniformity of interstellar chemistry is further brought out by van Dishoeck (12) in the study of protostellar regions within dense molecular clouds. There is exhibited a richness of conditions producing, for example, a highly nonstatistical isotopic distribu-

tions. The abundance ratio of  $ND_3$  to  $NH_3$  is near  $10^{-3}$  (13) compared with a cosmic D/H ratio of  $10^{-5}$ . In these cold regions, the polar species  $H_2D^+$  and even  $HD_2^+$  are observed. The recent laboratory observation of  $HD_2^+$  (14) was soon followed by its observation in cold prestellar cores (15). The primary destruction of  $H_3^+$  is by proton transfer to CO. In the very cold protostellar cores, CO is condensed onto the grains (12), allowing buildup of  $H_2D^+$ ,  $HD_2^+$ , and  $D_3^+$  by exchange reactions with HD. It is worth noting that CO is the second most abundant molecule following  $H_2$ . The canonical CO/ $H_2$  ratio is  $10^{-4}$ . Thus, HD is in actuality a relatively abundant species with HD/CO = 0.1. The importance of HD as a reactant is accentuated at low temperatures where the relative abundance of deuterium-containing isotopomers of  $H_3^+$  become abundant (16). These chemistries are discussed for the complex galactic center by Dalgarno (8).

The rich variety of observed species includes ions and free radicals. An interesting question is whether weakly bound complexes exist in the interstellar medium. Because these are routinely produced in the laboratory by adiabatic expansion of a high-pressure gas mixture, it might appear that they cannot be formed under the low-density interstellar conditions. Although these arguments sound persuasive, they ignore one essential difference between laboratory and interstellar chemistry, namely the much larger time scale available in interstellar space. In particular, radiative association is usually a slow process, which is unlikely to be of importance in laboratory conditions where gas densities of  $10^{11} \text{ cm}^{-3}$  or greater are typical. Clearly, laboratory measurement of the rate of slow radiative association reactions near 10 K are nonroutine (17).

Because the abundance of a collision complex will scale with the abundances of the collision partners, their collision frequency, and the binding energy of the complex, it appears that the most likely attractive species are an ion and  $H_2$ . The most abundant ion in dense molecular clouds is  $HCO^+$ . Thus, the species of interest initially is  $H_2 \cdot HCO^+$ . This complex is well characterized spectroscopically (18). The radiative association



was thought initially to proceed efficiently to the very stable protonated formaldehyde ion (6). It was shown, however, that instead the weakly bound isomer is formed (19). This species reacts with CO, forming the extremely interesting flux-

ional  $OC \cdot HCO^+$ . The proton tunneling frequency is estimated at  $564 \text{ cm}^{-1}$  (K. Higgins and Z. Yu, personal communication). A laboratory study of the infrared spectrum of this species is being pursued.<sup>†</sup> The exoergic reaction of this species with H atoms should yield  $H_2CO^+$ , the formaldehyde ion, a species not yet observed by microwave methods. Approximate rotational constants are known from high-resolution photoelectron spectroscopy (20), as well as electron structure computations (21, 22).  $H_2CO^+$  is a prolate asymmetric rotor, with small rotational constants B and C quite similar to the neutral formaldehyde species. The A rotational constant is almost 10% greater. At very low energies, formaldehyde ion is chemically unreactive with  $H_2$  (23) despite a number of exoergic reaction channels. The interstellar abundance of the formaldehyde ion, a semirigid free radical would provide insight into the role of weakly bound complexes in interstellar chemistries.

The richness of interstellar chemistry has been growing steadily in the variety of objects and regions observed. High-resolution spectroscopy has provided a relatively foolproof species-identification technique. It is almost surprising how few species misidentifications have occurred in the 40 years of molecular radioastronomy. Extremely elegant laboratory techniques have been invented to provide precise reference transition frequencies of interstellar molecules that are highly reactive, such as ions (7, 14, 24) and free radicals (25). The great value of extremely accurate rest frequencies is that they allow the spatial correlation of species by means of their coincident velocities along the line of sight. Although complete models of interstellar molecular abundances are difficult, more limited models that provide correlations between species are of considerable effectiveness. It is therefore essential that the regions viewed are common to the species being correlated.

The articles in this special feature provide a wide view of molecular astronomy and its underlying interstellar chemistry. For several years, PNAS has published special feature issues on many cutting edge research topics. Some of the themes of past special features have included: Gene Regulatory Networks, Social and Behavioral Sciences, Asymmetric Catalysis, Science and Technology for Sustainable Development, Long-Range Electron Transfer, and, most recently, Tissue Engineering and Cluster Chemistry and Dynamics.

<sup>†</sup>Linnartz, H., Workshop on Carbon in Space, Lake Como, Italy, May 23–25, 2006.

Scheduled for future issues of the journal are special features on Nitrogen Fixation, Polymerization, and Eukaryotic Transposable Elements and Genome Evolution. One objective of these special

features is to advance the journal's ongoing initiative to expand its coverage of the physical and social sciences and mathematics. PNAS continues to encourage and welcome research articles

in all areas of the natural and social sciences and mathematics.

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