# 1

# Interstellar molecules

## 1.1 Introduction

Our perception and understanding of the interstellar medium have been transformed over the last approximately 50 years. By the 1950s, optical and 21 cm radio measurements had demonstrated the presence of gas containing predominantly atomic hydrogen, together with a few atoms and ions (Na, K, $Ca^+$, $Ti^+$, Fe) that had absorption lines in the visible part of the spectrum. The gas was cold ($T \approx 100$ K) and had a number density $n(H) \approx 1$ cm$^{-3}$. 'Molecules' were represented by the radicals CH, $CH^+$ and CN, which have absorption bands in the visible. A dust component was known to be present, most directly from its obscuration of starlight. Over the last half-century, the construction of new telescopes, both ground-based and on board satellites, and rapid developments in receiver technology have led to over 100 molecular species being identified in the interstellar medium (see Table 1.1).

Foremost among the molecular species is the most abundant molecule in the Universe, $H_2$. Molecular hydrogen was first detected in absorption in the ultraviolet part of the spectrum, through its $X^1\Sigma_g^+ - B^1\Sigma_u^+$ Lyman electronic bands, by means of a sounding rocket [1]. It has since been observed at much higher spectral resolution by the Copernicus [2] and the FUSE [3] satellites. $H_2$ has also been observed in the far infrared by the *Infrared Space Observatory* (ISO) satellite [4], and through atmospheric windows in the near infrared. Thus, electronic, rotational and rovibrational transitions of $H_2$ have all been observed in the interstellar medium.

Cold $H_2$, at $T \lesssim 30$ K, maps the molecular clouds in galaxies but remains difficult to observe, being detectable only by means of ultraviolet electronic absorption lines in the Lyman and Werner ($X^1\Sigma_g^+ - C^1\Pi_u$) bands from above the Earth's atmosphere. Furthermore, a background continuum ultraviolet source, such as a hot star, is necessary for such observations. As scattering and absorption by dust are pronounced at short wavelengths, such observations are limited by the extinction along the line of sight through the molecular cloud and towards the star. Consequently, CO, which is the next most abundant interstellar molecule after $H_2$ [$n(CO)/n(H_2) \approx 10^{-4}$], has been used extensively as a tracer of molecular material. CO is readily observable from the ground at millimetre wavelengths; its longest wavelength rotational transition, $J = 1 \rightarrow 0$, falls at 2.6 mm. Indeed, radiative transitions between the low-lying rotational levels of CO are major contributors to the cooling of molecular clouds.

In this initial chapter, my aim is to summarize key aspects of our current understanding of the chemistry of the interstellar medium. We shall consider 'dense' (or 'dark') molecular clouds, whose interiors are shielded from the Galactic ultraviolet radiation field by dust absorption in the outer layers. This background radiation field owes its existence to hot (e.g. O and B) stars that emit in the ultraviolet. Although those photons beyond the H I

## 2 *Interstellar molecules*

Table 1.1. *Observed interstellar molecular species, ordered according to complexity, including isotopes and isomers (August 2004). Courtesy NRAO website: http://www.cv.nrao.edu/~awootten/allmols.html*

| Diatomic | Triatomic | 4-atoms | 5-atoms | 6-atoms | 7-atoms |
|---|---|---|---|---|---|
| $H_2$ | $C_3$ | c-$C_3H$ | $C_5$ | $C_5H$ | $C_6H$ |
| AlF | $C_2H$ | l-$C_3H$ | $C_4H$ | l-$H_2C_4$ | $CH_2CHCN$ |
| AlCl | $C_2O$ | $C_3N$ | $C_4Si$ | $C_2H_4$ | $CH_3C_2H$ |
| $C_2$ | $C_2S$ | $C_3O$ | l-$C_3H_2$ | $CH_3CN$ | $HC_5N$ |
| CH | $CH_2$ | $C_3S$ | c-$C_3H_2$ | $CH_3NC$ | $HCOCH_3$ |
| $CH^+$ | HCN | $C_2H_2$ | $CH_2CN$ | $CH_3OH$ | $NH_2CH_3$ |
| CN | HCO | $CH_2D^+$ | $CH_4$ | $CH_3SH$ | c-$C_2H_4O$ |
| CO | $HCO^+$ | HCCN | $HC_3N$ | $HC_3NH^+$ | $CH_2CHOH$ |
| $CO^+$ | $HCS^+$ | $HCNH^+$ | $HC_2NC$ | $HC_2CHO$ | |
| CP | $HOC^+$ | HNCO | HCOOH | $NH_2CHO$ | |
| CSi | $H_2O$ | HNCS | $H_2CHN$ | $C_5N$ | |
| HCl | $H_2S$ | $HOCO^+$ | $H_2C_2O$ | | |
| KCl | HNC | $H_2CO$ | $H_2NCN$ | | |
| NH | HNO | $H_2CN$ | $HNC_3$ | | |
| NO | MgCN | $H_2CS$ | $SiH_4$ | | |
| NS | MgNC | $H_3O^+$ | $H_2COH^+$ | | |
| NaCl | $N_2H^+$ | $NH_3$ | | | |
| OH | $N_2O$ | $SiC_3$ | | | |
| PN | NaCN | | | | |
| SO | OCS | | | | |
| $SO^+$ | $SO_2$ | | | | |
| SiN | c-$SiC_2$ | | | | |
| SiO | $CO_2$ | | | | |
| SiS | $NH_2$ | | | | |
| CS | $H_3^+$ | | | | |
| HF | SiCN | | | | |
| SH | AlNC | | | | |
| FeO | | | | | |

| 8-atoms | 9-atoms | 10-atoms | 11-atoms | 13-atoms | |
|---|---|---|---|---|---|
| $CH_3C_3N$ | $CH_3C_4H$ | $CH_3C_5N$ | $HC_9N$ | $HC_{11}N$ | |
| $HCOOCH_3$ | $CH_3CH_2CN$ | $(CH_3)_2CO$ | | | |
| $CH_3COOH$ | $(CH_3)_2O$ | $NH_2CH_2COOH$ | | | |
| $C_7H$ | $CH_3CH_2OH$ | $CH_3CH_2CHO$ | | | |
| $H_2C_6$ | $HC_7N$ | | | | |
| $CH_2OHCHO$ | $C_8H$ | | | | |
| $CH_2CHCHO$ | | | | | |

Lyman limit at 91.2 nm are absorbed, by atomic hydrogen, in the immediate vicinities of the hot stars, photons of longer wavelengths propagate into the general interstellar medium, where they are ultimately absorbed by either the dust or the gas. Accordingly, we shall also consider 'diffuse' (or 'translucent') clouds, which are traversed by this radiation field. The discussion will concentrate on reactions in the gas phase, although it is clear that grain-surface reactions are significant in the production of some species, notably $H_2$. Indeed, reactions between H atoms on the surfaces of grains are the only effective means of forming molecular hydrogen in the interstellar medium.

The only significant sources of ionization in dark clouds are cosmic rays and, possibly, X-rays in the vicinity of sources of such radiation. Cosmic rays with energies of a few MeV ionize hydrogen, producing 'secondary' electrons with energies of typically 30 eV [5]. The secondary electrons can collisionally excite the Lyman and Werner electronic transitions of $H_2$, leading to either the dissociation of the molecule or, more probably, to radiative cascade back to the electronic ground state; these processes are considered in Chapter 10. The fluorescence photons have wavelengths in the ultraviolet part of the spectrum and are sufficiently energetic to ionize and dissociate a number of species in the gas. The significance of this radiation field, generated *within* 'dark' clouds, was first recognized by Prasad and Tarafadar [6], and the photon spectrum was subseqently evaluated in detail [7].

## 1.2 Chemistry in interstellar clouds

### 1.2.1 Formation of molecular hydrogen

Even in the so-called 'dense' interstellar clouds, particle number densities are extremely low compared with those at atmospheric pressure, at which $n \approx 10^{19}$ cm$^{-3}$, and conditions are far from those in thermodynamic equilibrium at the kinetic temperature of the gas. Hydrogen exists predominantly in its 1s ground state, and collisions between hydrogen atoms can proceed along either of two potential energy curves, in which the electronic spins are either parallel (triplet state) or anti-parallel (singlet state). As the individual electronic orbital angular momenta are zero, the resultant orbital angular momentum and its projection on the internuclear axis of the quasi-molecule are also zero; the corresponding molecular states are denoted $^3\Sigma$ and $^1\Sigma$. As is well known from the Heitler–London theory of the $H_2$ molecule, the $^1\Sigma$ state is attractive whereas the $^3\Sigma$ state is repulsive. Figure 1.1 illustrates the variation of these potential energy curves with internuclear distance, $R$.

As the atoms are initially unbound, their total energy, $E$, is positive (the zero of the total energy is taken at the molecular dissociation limit). In order to stabilize, the system must lose energy and $E$ become negative. In the gaseous phase, this may occur:

- by means of three-body collisions, the third body taking away the excess energy, or
- by means of radiative processes.

Three-body collisions are extremely improbable at interstellar densities, and so the only way in which the system can stabilize is through the emission of a photon. However, transitions between the $^3\Sigma$ and $^1\Sigma$ electronic potential energy curves are forbidden to electric dipole radiation as they involve a change in the total spin quantum number. Radiative transitions involving the nuclear degrees of freedom (rotation and vibration) are also forbidden, as the $H_2$ molecule is homonuclear and does not possess a permanent dipole moment. (Radiative selection rules will be considered in Chapter 10). It follows that the formation of $H_2$ by two-body association in the gas phase cannot explain the observed presence of molecular hydrogen in the interstellar medium.

An alternative and still the only viable theory of $H_2$ formation in interstellar clouds is through grain-surface reactions [8]. The grain acts as a catalyst, playing the role of the third body in a three-body reaction. Early estimates of the rate of formation of $H_2$ on grains [9] suggested that most of the hydrogen would be expected to be in molecular form in dense molecular clouds.

4      *Interstellar molecules*
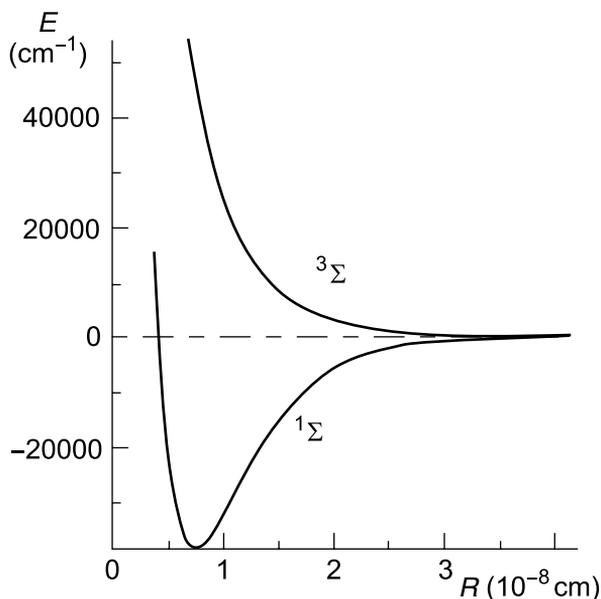


Figure 1.1  Electronic potential energy curves correlating with H(1s) + H(1s) at large internuclear separation $R$. The notation is $^{2S+1}\Lambda$, where $S = 0$ or 1 is the total electronic spin and $\Lambda$ is the projection of electronic orbital angular momentum on the internuclear axis. States with $\Lambda = 0$, as here, are denoted $\Sigma$.

In the more recent literature (e.g. [10]), a distinction has been made between the Eley–Rideal, or 'prompt', and the Langmuir–Hinshelwood, or 'diffusion', modes of formation of $H_2$ on grains. In the former case, the collision of an H atom from the gas with an H atom which is already physi-bound to the grain surface leads to the formation of $H_2$ and its release into the gas. In the latter case, the second H atom migrates across the grain surface by thermal hopping until it encounters and reacts with another H atom, releasing the molecule. It remains unclear whether one or the other of these mechanisms dominates. Also uncertain is the partition of the binding enery of the $H_2$ (4.48 eV) following the reaction, between translational, vibrational and rotational modes of the molecule and excitation of the phonon spectrum of the grain. Both experimental and theoretical work is continuing in an attempt to elucidate these issues. A recent theoretical study of the Eley–Rideal mechanism [11], in which the polycyclic aromatic hydrocarbon (PAH) coronene was assumed to be the substrate, indicates that most of the energy released in the reaction goes into vibrational excitation of the product molecule. These issues are important not only for the thermal balance of the medium – the kinetic energy of the $H_2$ is a significant heat source – but also for predictions of the spectrum of $H_2$ emitted from regions in which it forms, such as photon-dominated regions (PDRs) and behind dissociative shock waves propagating in molecular gas.

### 1.2.2      *Formation of molecules more complex than* $H_2$

Ion-neutral reactions play key roles in the formation of molecules in the interstellar medium. In the context of dense molecular clouds, such reactions were first discussed in detail by Herbst and Klemperer [12]. The long-range attraction, due to the polarization

of the molecule by the ion, ensures that these reactions are generally rapid at the low temperatures of the ambient medium, providing they are exothermic. In shocked molecular gas, the latter restriction no longer applies, owing to the higher kinetic temperature and, in magnetohydrodynamic shocks, to ion-neutral streaming associated with ambipolar diffusion (see Chapter 2).

**Dense clouds**

In dense molecular clouds, cosmic ray (cr) ionization of hydrogen is the primary ionization process,

$$H_2 + cr \rightarrow H_2^+ + e^- + cr \tag{1.1}$$

followed rapidly by

$$H_2^+ + H_2 \rightarrow H_3^+ + H \tag{1.2}$$

which yields $H_3^+$. The $H_3^+$ ion has a propensity to transfer a proton to neutral species with higher proton affinities than $H_2$. Heavier molecules may then be produced through a sequence of ion-neutral and dissociative recombination reactions:

$$H_3^+ + O \rightarrow OH^+ + H_2 \tag{1.3}$$

$$OH^+ + H_2 \rightarrow H_2O^+ + H \tag{1.4}$$

followed by

$$H_2O^+ + e^- \rightarrow OH + H \tag{1.5}$$

or

$$H_2O^+ + H_2 \rightarrow H_3O^+ + H \tag{1.6}$$

and

$$H_3O^+ + e^- \rightarrow H_2O + H \tag{1.7}$$

The hydroxyl radical and the water molecule are produced in this sequence of reactions. A similar sequence, initiated by

$$H_3^+ + C \rightarrow CH^+ + H_2 \tag{1.8}$$

generates the carbon-bearing species CH, $CH_2$, $CH_3$ and $CH_4$. Dissociative recombinations such as (1.5) and (1.7) are generally rapid, owing to the long-range coulomb attraction between the reactants involved and the low mass of the electron, which ensures a high collision frequency.

Oxidation of the products of the above hydrogenation reactions results in the formation of CO, e.g.

$$CH + O \rightarrow CO + H \tag{1.9}$$

and $O_2$ can form in the reaction

$$OH + O \rightarrow O_2 + H \tag{1.10}$$

Both OH and $O_2$ react with C to produce CO. In oxygen-rich environments ($n_O > n_C$), most of the carbon is converted into CO when molecules form.

Observations with the *Submillimeter Wave Astronomy Satellite* (SWAS) satellite [13, 14] have shown that $H_2O$ and $O_2$ are much less abundant in dense clouds than expected on the basis of gas-phase chemical models. At least some of these molecules are expected to be frozen on to the grains at the low temperatures that prevail in such clouds.

Unlike the corresponding reactions involving C and O, the protonation of N by $H_3^+$ is endothermic and has a negligible rate at low kinetic temperatures, $T$. Molecular nitrogen is believed to be produced in the reaction

$$N + OH \rightarrow NO + H \tag{1.11}$$

followed by

$$NO + N \rightarrow N_2 + O \tag{1.12}$$

Proton transfer from $H_3^+$ to $N_2$ then yields the molecular ion $N_2H^+$. $N_2$ can also react with $He^+$, which is produced by cosmic-ray ionization of He:

$$He^+ + N_2 \rightarrow N^+ + N + He \tag{1.13}$$

This may be followed by the slightly endothermic reaction

$$N^+ + H_2 \rightarrow NH^+ + H \tag{1.14}$$

which initiates a sequence of hydrogenation reactions with $H_2$, terminating at $NH_4^+$. At low $T$, reaction (1.14) is driven principally by ortho-$H_2$, whose ground state lies approximately 170 K above that of para-$H_2$ and increases the enthalpy of the reactants by the corresponding amount.[1] The dissociative recombination of $NH_4^+$

$$NH_4^+ + e^- \rightarrow NH_3 + H \tag{1.15}$$

produces ammonia, $NH_3$.

Ammonia can be produced also on grains and be subsequently released into the gas phase. Reactions on grain surfaces are believed to occur predominantly with adsorbed H, which, being light, can migrate relatively rapidly across the grain surface. The saturated (in hydrogen) species $CH_4$, $NH_3$ and $H_2O$ can form in this way.

Atomic sulphur reacts with $H_3^+$, producing $SH^+$. However, the reactions of $SH^+$ and $H_2S^+$ with $H_2$ are endothermic and proceed with negligible rates in cold gas. $SH^+$ may undergo (slow) radiative association with $H_2$

$$SH^+ + H_2 \rightarrow H_3S^+ + h\nu \tag{1.16}$$

---

[1] The energies of the reactants and the products of a reaction are expressed as *enthalpies* and often given in units of kcal $mol^{-1}$ (1 kcal $mol^{-1} \equiv 503.4$ K); units of kJ $mol^{-1} \equiv 120.3$ K are also used.

and $H_2S$ and SH are produced in the subsequent dissociative recombination of $H_3S^+$. On the other hand, $SH^+$ may also undergo charge transfer with S

$$SH^+ + S \rightarrow SH + S^+ \tag{1.17}$$

and SH reacts with O

$$SH + O \rightarrow SO + H \tag{1.18}$$

and SO reacts with C

$$SO + C \rightarrow CS + O \tag{1.19}$$

CS is recognized as a tracer of dense, cold gas. Unlike CO, the compound of carbon with the corresponding element (O) in the the second row of the Periodic Table, CS has a large permanent dipole moment. As a consequence, the populations of the rotational energy levels of CS begin to thermalize at densities that are two orders of magnitude higher than is the case for CO. The populations of the excited states increase quadratically with the gas density below the critical density, at which the rates of radiative and collisional de-excitation become equal, but only linearly above the critical density. Thus, the emission from CS increases, relative to the emission from CO, at gas densities higher than the critical density for CO, but lower than the critical density for CS. The chemical routes to simple interstellar molecules, outlined above, are shown in Fig. 1.2.

In dense clouds, $H_3^+$ reacts mainly with CO:

$$H_3^+ + CO \rightarrow HCO^+ + H_2 \tag{1.20}$$

However, there is indirect observational evidence that, in protostellar cores, where the temperature may be very low ($T \lesssim 10$ K), essentially all molecules containing species heavier than He may have frozen on to the grains. Under these circumstances, HD (which, like $H_2$, forms on the surfaces of grains) may participate in the sequence of reactions

$$H_3^+ + HD \rightarrow H_2D^+ + H_2 \tag{1.21}$$

$$H_2D^+ + HD \rightarrow D_2H^+ + H_2 \tag{1.22}$$

and

$$D_2H^+ + HD \rightarrow D_3^+ + H_2 \tag{1.23}$$
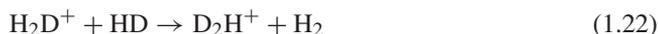
which can result in high degrees of *fractionation* of deuterium, i.e. enhanced fractional abundances of the the deuterated isotopes of $H_3^+$, relative to the elemental abundance ratio $n_D/n_H$. Fractionation occurs because the zero-point vibrational energies of successive ions in the reaction sequence, $H_3^+$, $H_2D^+$, $D_2H^+$ and $D_3^+$, decrease owing to the increase in their masses. At such low temperatures, the extent of the fractionation might be such that $D_3^+$ is the most abundant ion in the gas.

8        *Interstellar molecules*
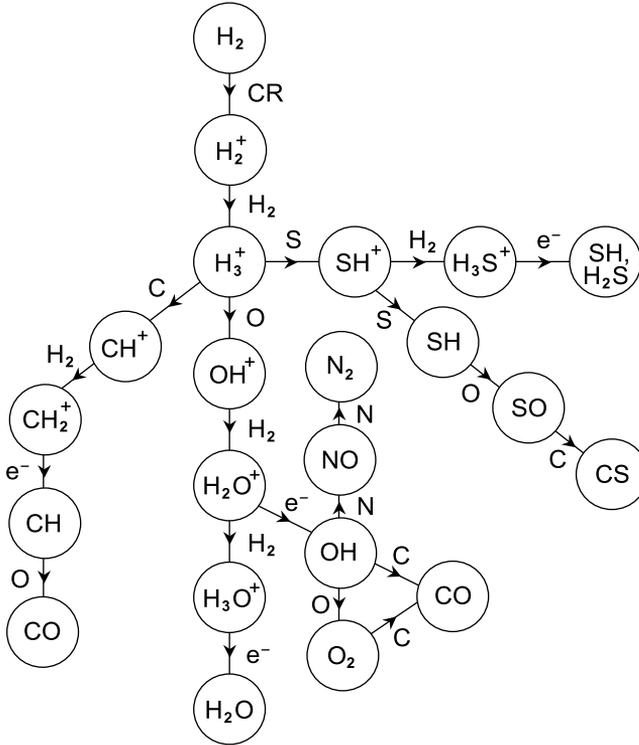


Figure 1.2  Chemical routes to simple interstellar molecules in dense molecular clouds.

### Diffuse clouds

The diffuse interstellar gas is permeated by photons with energies $h\nu < 13.6$ eV, the ionization potential of atomic hydrogen. Consequently, atoms with lower ionization potentials, such as C, Si, S and Fe, are photoionized. This process not only modifies the reactants available to form molecules in the gas phase but also produces a higher fractional abundance of electrons. Furthermore, some of the molecules and radicals that are formed can be dissociated, or even ionized, by the background radiation field. The energy input from the radiation field leads to higher kinetic temperatures ($T \approx 80$ K) than those prevailing in dark clouds.

The ionization potential of atomic oxygen is higher than that of atomic hydrogen, but by only a small amount, equivalent to 227 K. The charge transfer of O with $H^+$, which is produced by cosmic ray ionization of H,

$$H^+ + O \rightarrow H + O^+ - 227 \text{ K} \tag{1.24}$$

is consequently endothermic by 227 K but nonetheless proceeds quite rapidly in diffuse clouds. The hydrogen abstraction reaction with $H_2$

$$O^+ + H_2 \rightarrow OH^+ + H \tag{1.25}$$

then initiates the same sequence which occurs in dense clouds [reactions (1.4)–(1.7) above]. The corresponding reaction of $C^+$ with $H_2$

$$C^+ + H_2 \rightarrow CH^+ + H - 4640 \text{ K} \tag{1.26}$$

has a large endothermicity (4640 K). It has been proposed that $CH^+$ forms in shocked gas, as a consequence of interstellar turbulence, or as a result of diffusion. None of these proposals has proved completely successful in accounting for both the observed column densities and the line profiles and shifts of $CH^+$ and its associated radical, CH.

## 1.3    Chemical bistability in dense clouds

The chemical composition of molecular gas attains steady state if the chemical timescales are shorter than the dynamical and other relevant timescales that characterize the medium. The assumption of steady state provides a point of reference, but the abundances of some of the chemical species in dark clouds are unlikely to reach a time-independent equilibrium. Under these circumstances, their current abundances depend on their 'initial' values.

Even if steady state has been attained, it does not guarantee that the abundances are independent of the initial conditions. The first suggestion that abundances in steady state may depend on the initial conditions is to be found in the work of Graedel *et al.* [15], who discovered the existence of two distinct chemical phases. This discovery remained neglected for a decade, partly as a consequence of the belief at that time in a very low value for the coefficient of dissociative recombination of $H_3^+$ with electrons – a belief which subsequent experimental work [16, 17] showed to be unfounded. As we have already seen, $H_3^+$ plays a pivotal role in interstellar chemistry, and its rate of recombination with electrons is crucially important. The two chemical phases were rediscovered in the early 1990s [18], and subsequent work [19] demonstrated the relevance of the phenomenon of bistability to the chemistry of dark clouds.

'Bistability', or chemical hysteresis, is analogous to the phenomenon of magnetic hysteresis in ferromagnetic materials. The degree of ionization in the steady state of gas with densities representative of dark clouds is plotted in Fig. 1.3; each point in this figure is a steady-state solution. The solutions display an unstable branch, between the points A and B, and two stable branches, which are labelled 'HIP' and 'LIP' for the high and the low ionization phases, respectively. In the range of gas density $2 \times 10^3 \leq n_H \leq 2 \times 10^4$ cm$^{-3}$, bistability occurs. The degree of ionization is approximately an order of magnitude greater in the HIP than in the LIP.

The difference in the degree of ionization in the HIP and LIP is reflected in the abundances of many atomic and molecular species. For example, the corresponding values of the ratio $n(C)/n(CO)$ are plotted in Fig. 1.4; this ratio is of the order of $10^{-1}$ in the HIP but less than $10^{-2}$ in the LIP.

An alternative and instructive way of presenting the results is illustrated in Fig. 1.5, which shows $n(O_2)$ plotted agains $n(C)$ for models in which $n_H = 2 \times 10^4$ cm$^{-3}$. In steady state, the LIP solution yields a relatively high molecular oxygen and low atomic carbon abundance, and vice versa for the HIP solution. Slightly different initial conditions can lead to the the opposite (LIP or HIP) solution prevailing in steady state. Thus, small variations in parameters

10      *Interstellar molecules*
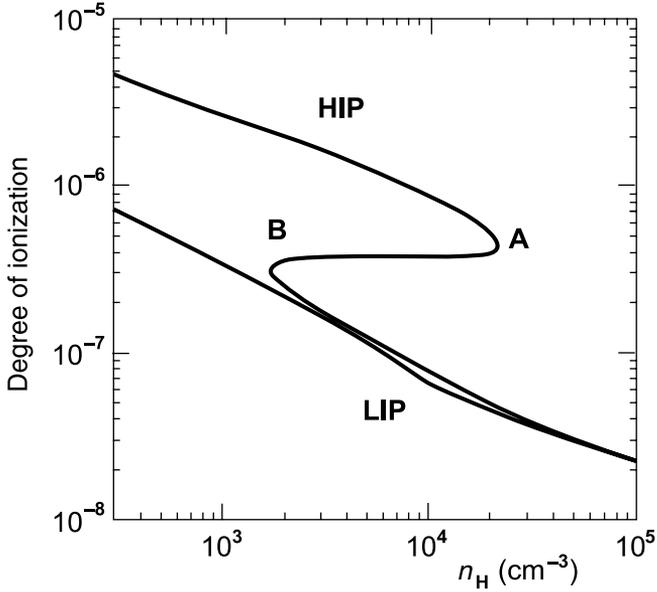


Figure 1.3    Degree of ionization of interstellar gas, computed in steady state, for a range of values of the gas density $n_H \approx n(H) + 2n(H_2)$. The high and low ionization phases are indicated. The curve has an unstable branch between points A and B, where it displays the phenomenon of bistability.
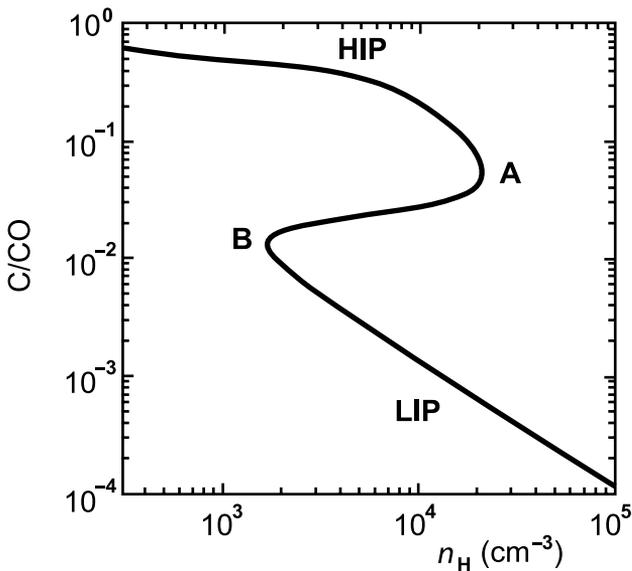


Figure 1.4    Bistability in the variation of $n(C)/n(CO)$ with $n_H$.