Chapter 2 Molecular clouds

This chapter lays the foundation for understanding the physics and chemistry of the material from which stars eventually form. Molecular clouds are a dense component of the interstellar medium and they comprise about 50% of the total interstellar gas of a galaxy. The following sections summarize first some observational aspects of molecular clouds, such as their sizes, appearance at various wavelength and in various tracers, and their constituents. We then move to learning some fundamental molecular physics of simple molecules such as H₂ and CO and how to understand the origin of molecular lines. The third section focuses on the various heating and cooling processes in a molecular cloud that govern the energy balance of the dust and gas. This topic will be picked up in a later chapter on irradiated disks, where we will encounter a similar set of heating and cooling processes. The last section gives a brief introduction into astrochemistry, introducing the basic principles of chemistry in space. We discuss there the chemical composition of molecular clouds. Also the astrochemistry will come back at a later stage when we talk about the chemistry of protoplanetary disks.



Figure 2.1: The Eagle Nebula at a distance of 1800 pc viewed with HST/ACS in 2004. The structure is about 9.5 ly (\sim 3 pc) high.

2.1 Observational properties of molecular clouds

A cloud is a region of the interstellar medium with densities larger than $10 - 30 \text{ cm}^{-3}$. Diffuse clouds can have somewhat lower densities. Clouds move through the galaxy as entities. However, they are generally not spherical, but rather irregular with filamentary structures (Fig. 2.1). Depending on their extinction, A_V , these clouds are more or less transparent to the interstellar UV radiation coming from the hot O and B stars in our galaxy. At an extinction larger than $A_V \sim 0.5$, most of the hydrogen is in molecular form. Table 2.1 lists the typical properties of molecular clouds found from studies within our own galaxy. We will focus in the following on some of the examples listed in the last column to illustrate the appearance and properties of these clouds.

Table 2.1: Physical properties of molecular clouds (from Stahler & Palla 2004)

| Cloud type | A_V | $n_{ m tot}$ | L | T | M | Example |
|--------------------------|-------|--------------|------|-----|---------------------|------------------|
| | [mag] | $[cm^{-3}]$ | [pc] | [K] | $[{\rm M}_{\odot}]$ | |
| Diffuse | 1 | 500 | 3 | 50 | 50 | ζ Ophiuchi |
| Giant Molecular Cloud | 2 | 100 | 50 | 15 | 10^{5} | Orion |
| Dark Clouds | | | | | | |
| Complexes | 5 | 500 | 10 | 10 | 10^{4} | Taurus-Auriga |
| Individual | 10 | 10^{3} | 2 | 10 | 30 | B1 |
| Dense Cores/Bok Globules | 10 | 10^{4} | 0.1 | 10 | 10 | TMC-1/B335 |

2.1.1 Dust and gas in clouds

As the interstellar medium, molecular clouds also consist of gas and dust with a typical mass ratio of 100. The dust in these regions is typically cold and can thus be detected through its thermal emission at submm and mm wavelength. At those wavelength, the extinction is very low and the emission can be optically thin. If that is the case, the observations trace the total dust mass residing in the molecular cloud. However, for accurate mass determinations, the dust emissivity needs to be known and the typical uncertainty can be up to a factor 3.

Most of the gas is in the form of molecular hydrogen. However, as we will see later in this chapter, H₂ as a symmetric molecule does not possess a permanent dipole moment. Hence, the infrared transitions are forbidden and intrinsically weak which makes it difficult to observe H_2 . The second most abundant molecule is CO and that one has a rich spectrum of rotational lines that are easily excited at the low temperatures of these clouds. The ground rotational transition for example has an excitation temperature of 5 K and a wavelength of 2.6 mm. The rotational lines have very high Einstein A coefficients and low critical densities $(n_{\rm cr} < 10^4 {\rm cm}^{-3})$, the critical density is the one, where collisional rates populating and depopulating a particular energy level dominate over radiative rates), which means that they are generally in LTE, but also that they are very optically thick. A way out is to use CO isotopes such as



Figure 2.2: Sky map for Taurus-Auriga region. CO column densities from Ungerechts and Thaddeus (1987) are shown as dotted lines for flux densities of 3, 5, 10, 25 and 40 K km s⁻¹. Open triangles indicate the positions of optically visible T Tauri stars, while core sources from the Beichman et al. (1986) and Myers et al. (1987) surveys are plotted as open squares. The new IRAS sources discussed in this paper are indicated by stars (new class I sources), filled triangles (new TTS), or large crosses (galaxies and apparent field stars). The position of some objects have been offset for clarity (caption and figure from Kenyon et al. 1990).

 ${}^{13}C^{16}O$ and ${}^{12}C^{18}O$, which are a factor 60 and 500 lower in abundance than the main isotope ${}^{12}C^{16}O$. All these lines can be easily observed with ground-based radio telescopes. Gas line observations also have the advantage that they carry kinematic information about the velocity field in the cloud (line profile and width of the line). In addition, magnetic field strength can be measured through the Zeeman splitting of molecular lines.

2.1.2 Low mass star forming clouds

Fig. 2.2 shows a map of the CO molecular emission (J=1-0) in the Taurus-Auriga molecular cloud ($d \sim 140 \text{ pc}$). Taurus-Auriga is a low-mass star forming region, i.e there are no massive O and B stars forming that irradiate the molecular gas. The total gas mass in this region is $\sim 10^4 \text{ M}_{\odot}$. The figure nicely shows how the young stars are scattered throughout the entire cloud complex. The sensitivity of this IRAS (Infrared Astronomical Satellite) survey allowed the detection of young stars brighter than 0.5 L_{\odot}. More recently, Spitzer observations provided much deeper observations, hence a larger sensitivity for the detection of young stellar objects.



Figure 2.3: The spatial distribution of all Spitzer identied infrared excess sources from the combined IRAC and 2MASS photometry of Orion A (left), Orion B (right) and Ophiuchus (bottom center). The contours outline the Bell Labs ¹³CO maps for the Orion A and B clouds (Bally et al., 1987; Miesch and Bally, 1994), and an A_V map of Ophiuchus (Huard, 2006). The large grey dots are the sources with infrared excesses (caption and figure from Allen et al. 2007).

2.1.3 High mass star forming clouds

Fig. 2.3 shows the distribution of infrared-excess (likely YSOs) sources in the Orion star forming cloud $(d \sim 400 \text{ pc})$. This is a Giant Molecular Cloud (GMC), where high mass stars (O and B-type stars) haven been forming within the last 10^6 yr. These hot stars emit strongly in the UV spectral range, thereby heating and ionizing the surrounding gas. Over time, they created the Orion nebula (M42). The nebula has recently also being surveyed by the Hubble Space Telescope to provide a legacy dataset for improving our

understanding of star formation theory (Robberto et al. 2009). The small grey dots in Fig. 2.3 show all the detections in the Spitzer 3.6 and 4.5 μ m bands with magnitudes brighter than 15 and the large grey dots are those that show an infrared excess. The black circles/triangles are sources that have been associated with a cluster (the two symbols are alternated so that neighboring clusters can be differentiated).

2.1.4 Cores and clumps

As the previous sections documented, molecular clouds are highly fragmented and consists of smaller entities, the clumps and cores. Clumps are generally the larger substructures in molecular clouds, having typical sizes of 1 pc. They are the precursors of stellar clusters. Cores are about a factor 10 smaller and have even higher densities. They are assumed to be gravitationally bound and will collapse to form individual stars or binaries.

The clumpy structure of molecular clouds is shown to partially originate from supersonic motions in the ISM. In some cases, the clumps seem to be rather confined by the pressure from the surrounding medium and thus not in virial equilibrium. In that sense, not every clump will eventually form stars.

The clump masses within molecular clouds have been studied via CO isotope observations. Above a certain minimum mass, the clump mass spectrum follows a power law

$$\frac{dN}{dM} \propto M^{-1.6...1.8}$$

$$\Rightarrow \frac{MdN}{dM} \propto M^{-0.6...0.8} .$$
(2.1)

This means that most of the mass is actually in massive clumps. Fig. 2.4 shows such a clump mass spectrum for the Rosette molecular cloud, where a minimum mass of $\sim 30 \ M_{\odot}$ has been adapted. Combining this with extinction measurements, it can be shown that even though the clumps seem to fill the plane of the molecular cloud on the sky, they do not fill the volume of the cloud.

Most clumps however do not form stars. Hence, the mass spectrum of cores is more relevant in understanding the mass distribution of newly forming stars. While the star formation efficiency of an entire molecular cloud is only of the order of a few %, cores have a much higher efficiency of ~ 30 - 40 %. Fig. 2.6 shows a deep 1.3 mm continuum map of ρ Ophiuchi (d = 140 pc) with a resolution of 0.01 pc (~ 2000 AU). This large survey produced a core mass spectrum that can be splitted into two power law regimes, one for



Figure 2.4: Distribution of clump masses in the Rosette Molecular Cloud (caption and figure from Stahler & Palla 2004).



Figure 2.5: Frequency distribution of masses for 60 small-scale clumps extracted from the mosaic of Fig. 2.6 (solid line). The dotted and long-dashed lines show power laws of the form $\Delta N/\Delta m \propto m^{-1.5}$ and $\Delta N/\Delta m \propto m^{-2.5}$, respectively. The error bars correspond to \sqrt{N} counting statistics (figure and caption from Motte et al. 1998).



Figure 2.6: Millimeter continuum mosaic of the ρ Oph main cloud including the dense cores Oph-A, Oph-B1, Oph-B2, Oph-C, Oph-D, Oph-E, and Oph-F. The data were smoothed to an effective angular resolution of 15" (HPBW). Contour levels go from 5 to 40 MJy/sr with steps of 5 MJy/sr, from 50 to 80 MJy/sr by 10 MJy/sr, 100 MJy/sr and from 120 to 280 MJy/sr with steps of 40 MJy/sr (1 MJy/sr \simeq 6 mJy/15"-beam). The mean rms noise level is \sim 1.2 MJy/sr. Note the remarkable linear chain of clumps and embedded YSOs in the southern part of the C¹⁸O ridge (emphasized by a white straight line). Figure and caption from Motte et al. (1998).

 $M < 0.5 M_{\odot}$ and one for $M > 0.5 M_{\odot}$. They have power law indices of -1.6 and $-2.1 \dots -2.5$, respectively (see Fig. 2.5).

2.1.5 The Initial Mass Function

As part of our understanding of star formation, it is important to understand the mass distribution of entire groups of newly forming stars. We already know that massive hot O and B stars are much rarer than solar-type stars and that most stars in the Milky Way are in fact stars with a mass much lower than that of our Sun. We can study this quantitatively by looking for example at stars in stellar clusters. The core mass spectrum found in the previous section resembles largely the initial mass function found for newly born stars.

2.2 Molecular Cloud Stability

We will now try to understand the basic stability energy content and stability of molecular clouds.

2.2.1 The Jeans mass

Lets assume that a molecular cloud is a static and homogeneous medium that satisfies the equations of continuity, Euler's equation, and Poisson's equation

$$\frac{\partial \rho_0}{\partial t} + \rho_0 \nabla \cdot \mathbf{v}_0 = 0 \tag{2.2}$$

$$\frac{\partial \left(\rho_0 \mathbf{v}_0\right)}{\partial t} + \nabla \cdot \left(\rho_0 \mathbf{v}_0 \mathbf{v}_0 + P_0\right) = 0 \tag{2.3}$$

$$\nabla^2 \Phi_0 = 4\pi G \rho_0 \tag{2.4}$$

We also assume that the ideal gas law holds: $P_0 = \rho_0 hT/(\mu m_p) = \rho_0 c_s^2$. We assume that this medium is initially at rest, i.e. $\mathbf{v}_0 = 0$, and that it is infinitely extended, i.e. $\Phi_0 = 0$. We consider a small perturbation from the initial state

$$\rho = \rho_0 + \rho_1 \qquad \mathbf{v} = \mathbf{v}_1 \qquad \Phi = \Phi_1 \tag{2.5}$$

We now insert the perturbed quantities into eqs (2.2)–(2.4) and make use of the fact that the unperturbed quantities are solutions of the equations, and we neglect terms that we quadratic in the perturbations. After some algebra we find

$$\frac{\partial \rho_1}{\partial t} + \rho_0 \nabla \cdot \mathbf{v}_1 = 0 \tag{2.6}$$

$$\frac{\partial \mathbf{v}_1}{\partial t} = -\nabla \Phi_1 - \frac{\nabla P_1}{\rho_0} \tag{2.7}$$

$$\nabla^2 \Phi_1 = 4\pi G \rho_1 \tag{2.8}$$

We now take the time derivative of eq. (2.6), eliminate $\partial \mathbf{v}_1 / \partial t$ usinf eq. (2.7). Then we insert eq.(2.8) and eliminate the pressure using the ideal gas law. In this way we arrive at a wave equation for the density perturbation

$$\frac{\partial^2 \rho_1}{\partial t^2} - 4\pi G \rho_0 \rho_1 + \frac{kT}{\mu m_p} \nabla^2 \rho_1 = 0$$
(2.9)

which we attempt to solve using a plane wave Ansatz $\rho_1 = \exp\left(i\left(\frac{2\pi x}{\lambda} - \omega t\right)\right)$. Inserting this Ansatz into eq.(2.9) we find the following dispersion relation:

$$\omega^2 = \left(\frac{2\pi}{\lambda}\right)^2 \left(\frac{kT}{\mu m_p}\right) - 4\pi G\rho_0 \tag{2.10}$$

This results indicates that perturbations on lengths scales larger than the Jeans Length

$$\lambda_J = \left(\frac{\pi kT}{\mu m_p G \rho_0}\right) \tag{2.11}$$

will grow exponentially, while smaller perturbations will be damped. Since this instability occurs in all three spatial coordinates, a sphere with diameter λ_J defines the maximum stable mass, the *Jeans mass*

$$M_J = \frac{\pi}{6} \rho_0 \left(\frac{\pi kT}{\mu m_p G \rho_0}\right)^{3/2} \tag{2.12}$$

2.2.2 The problem of star formation efficiency

The galaxy should be wildly gravitationally unstable, because all molecular clouds are above the Jeans mass limit derived in the previous section. If we consider the free fall time scale (we will derive it later) $t_{\rm ff} = \sqrt{\frac{3\pi}{32G\rho}}$ for the interstellar medium with an average density of 17 hydrogen atoms per cm³, then we find a free fall time of 8×10^6 years. The entire molecular gas in the milkyway (about $2 \times 10^{10} M_{\odot}$) should be converted into stars in a free fall time scale. The expected star formation rate is therefore $\sim 250 M_{\odot}/{\rm yr}$, while the observed star formation rate is only 3 solar masses per year. Something is slowing dwn star formation!

2.2.3 The Virial theorem for clouds

A general form of the Viral theorem can be derived from the momentum equation of magneto-hydrodynamics

$$\rho \frac{D\mathbf{v}}{Dt} = -\nabla P - \rho \nabla \Phi + \frac{1}{c} \mathbf{j} \times \mathbf{B}$$
(2.13)

with $D\mathbf{v}/Dt := (\partial v/\partial t)_x + \nabla \cdot (\mathbf{vv})$. Using Maxwells equation $\nabla \times \mathbf{B} = 4\pi \mathbf{j}/c$, we get

$$\rho \frac{D\mathbf{v}}{Dt} = -\nabla P - \rho \nabla \Phi + \frac{1}{4\pi} (\mathbf{B} \times \nabla) \mathbf{B} - \frac{1}{8\pi} \nabla \left| \mathbf{B}^2 \right|$$
(2.14)

This equation describes the local behavior of the fluid. Multiplying by \mathbf{r} (scalar product) and integrating over the entire volume, also using the continuity equation leads to

$$\frac{1}{2}\frac{\partial^2 I}{\partial t^2} = 2\mathcal{T} + 2\mathcal{U} + \mathcal{W} + \mathcal{M} \qquad \text{with} \qquad (2.15)$$

$$I = \int \rho \left| r^2 \right| d^3x \qquad \text{moment of inertia} \qquad (2.16)$$

$$\mathcal{T} = \frac{1}{2} \int \rho \left| v^2 \right| d^3 x \qquad \text{kinetic energy} \qquad (2.17)$$

$$\mathcal{U} = \frac{3}{2} \int P d^3 x \qquad \text{thermal energy} \qquad (2.18)$$

$$\mathcal{W} = \frac{1}{2} \int \rho \Phi d^3 x \qquad \text{gravitational energy} \qquad (2.19)$$
$$\mathcal{M} = \frac{1}{8\pi} \int B^2 d^3 x \qquad \text{magnetic energy} \qquad (2.20)$$

Long term stability means that the overall mass distribution and size does not change, i.e. that the moment of inertia does not change with time. As the LHS of eq. (2.15) vanished, we find $2\mathcal{T} + 2\mathcal{U} + \mathcal{W} + \mathcal{M} = 0$. We can now use observed values for temperature T, kinetic (turbulent) motions V, cloud mass M and radius R, and magnetic fields B, and compare the different energies:

$$\frac{\mathcal{U}}{|\mathcal{W}|} \approx \frac{MRT}{\mu m_p} \left(\frac{R}{GM^2}\right) = 0.003 \qquad \left(\frac{M}{10^5 M_{\odot}}\right)^{-1} \left(\frac{R}{25 \text{pc}}\right) \left(\frac{T}{15K}\right) \tag{2.21}$$

$$\frac{\mathcal{M}}{|\mathcal{W}|} = \frac{B^2 R^3}{6\pi} = 0.3 \qquad \left(\frac{B}{20\mu G}\right)^2 \left(\frac{R}{25pc}\right)^4 \left(\frac{M}{10^5 M_{\odot}}\right)^{-2} \tag{2.22}$$

$$\frac{\mathcal{T}}{|\mathcal{W}|} \approx \frac{1}{2} M \Delta V^2 \frac{R}{GM^2} = 0.5 \qquad \left(\frac{\Delta V}{4\text{km/s}}\right)^2 \left(\frac{M}{10^5 M_{\odot}}\right)^{-1} \left(\frac{R}{25 \text{pc}}\right)$$
(2.23)

So while thermal energies are much to low to counter gravity, both magnetic fields and kinetic (turbulent) motions contain energies that are of the same order as the gravitational energy. We conclude that magnetic fields and turbulence are keeping molecular clouds from collapsing in their entirety.

2.3 Line emission from molecules

The first molecules were detected in space in the late 1930's through their absorption lines in the spectra of background stars. Among the first were CH, CH^+ and CN. As laboratory experiments provided more accurate line frequencies, the field exploded leading to what we call now Astrochemistry. The chemical viewpoint of how these molecules form in the first place will be covered in Sect. 2.5. Here we focus first on understanding the spectra of molecules.

Figure 2.7 provides an overview table of some of the most relevant molecules in space. It shows the wavelengths at which these molecules are observed, the type of transition and also the temperatures required

Figure 2.7: Some astrophysically relevant molecules (taken from Stahler & Palla 2004).

| molecule | abundance ^a | transition | type | λ | T^b_{\circ} (K) | A_{ul} (s ⁻¹) | $n_{ m crit}^c$ (cm ⁻³) | comments |
|----------------|-------------------------|-----------------------------|---------------------|--------|-------------------|--------------------------------|--|----------------------|
| H ₂ | 1 | 1→0 S(1) | vibrational | 2.1 µm | 6600 | 8.5×10 ⁻⁷ | 7.8×10 ⁷ | shock tracer |
| CO | 8×10^{-5} | $J=1 \rightarrow 0$ | rotational | 2.6 mm | 5.5 | 7.5×10^{-8} | 3.0×10^{3} | low density probe |
| ОН | 3×10^{-7} | $^{2}\Pi_{3/2};J=3/2$ | Λ -doubling | 18 cm | 0.08 | 7.2×10^{-11} | 1.4×10^{0} | magnetic field probe |
| NH_3 | 2×10^{-8} | (J,K)=(1,1) | inversion | 1.3 cm | 1.1 | 1.7×10^{-7} | 1.9×10^4 | temperature probe |
| H_2CO | 2×10^{-8} | $2_{12} \rightarrow l_{11}$ | rotational | 2.1 mm | 6.9 | 5.3×10^{-5} | 1.3×10^{6} | high density probe |
| CS | 1×10^{-8} | $J=2 \rightarrow l$ | rotational | 3.1 mm | 4.6 | 1.7×10^{-5} | 4.2×10^{5} | high density probe |
| HCO^+ | 8×10^{-9} | $J{=}1\rightarrow 0$ | rotational | 3.4 mm | 4.3 | 5.5×10^{-5} | 1.5×10^5 | tracer of ionization |
| H_2O | | $6_{16} \rightarrow 5_{23}$ | rotational | 1.3 cm | 1.1 | 1.9×10^{-9} | 1.4×10^3 | maser |
| " | $<\!\!7 \times 10^{-8}$ | $1_{10} \rightarrow 1_{11}$ | rotational | 527 µm | 27.3 | 3.5×10^{-3} | 1.7×10^{7} | warm gas probe |

^a number density of main isotope relative to hydrogen, as measured in the dense core TMC-1

^b equivalent temperature of the transition energy; $T_{\circ} \equiv \Delta E_{\rm ul}/k_B$

 c evaluated at T=10 K, except for H2 (T=2000 K) and H2O at 527 μm (T=20 K)

for exciting those transitions. The last column indicates which type of information those transitions carry. Column 7 gives the transition probability A_{ul} (The Einstein A coefficient for spontaneous emission) for the line and column 8 lists the critical density. The latter is defined as

$$n_{\rm crit} = \frac{A_{ul}}{\gamma_{ul}} \quad , \tag{2.24}$$

which is the ratio between downward radiative rates $(A_{\rm ul})$ and collisionally induced downward transitions $(\gamma_{\rm ul})$, where *u* denotes the upper level and *l* the lower level). This critical density indicates the minimum density required to achieve LTE level populations, i.e. energy levels populated according to the Boltzmann equation at the local ambient temperature. Hence, at densities $n > n_{\rm crit}$, the de-population of the upper level occurs preferentially through collisions. In a two-level system without radiative excitation, the equation of statistical equilibrium would read as

$$n_i n_x \gamma_{lu} = n_x n_u \gamma_{ul} + n_u A_{ul} \quad . \tag{2.25}$$

Here, n_i is the density of the molecule we consider and n_x is the density of the collision partner (e.g. electrons, neutral or molecular hydrogen). The two terms on the right hand side are due to collisional de-excitation and radiative de-excitation. The critical density is then defined as the one where these two are equal.

Homonuclear molecules, i.e. molecules that consist of two or more equal atoms (e.g. H_2), do not possess a permanent dipole moment. The dipole moment is generated through the slight dif-



Figure 2.8: Rotational levels of H₂ for the first two vibrational states. Within the v = 0 state, the J = 2 - 0 transition at 28.2 μ m is displayed. Also shown is the transition giving the 1 - 0 S(1) ro-vibrational line at 1.12 μ m. Note that two different energy scales are used (caption and figure from Stahler & Palla 2004).

ference in electronegativity between the constituents of a molecule. This slight difference in electronegativity

allows one of the atoms to pull the 'cloud of electrons' closer than the other, hence inducing a slight shift in charge.

A molecule has various degrees of freedom. It can rotate, vibrate or be electronically excited. Its total energy is thus

$$E_{\rm tot} = E_{\rm rot} + E_{\rm vib} + E_{\rm elect} \quad . \tag{2.26}$$

Generally, the rotational levels have the lowest energies, followed by the vibrational energy levels and then by the electronic states. However, at some point the highly rotational excited levels of a particular vibrational state can overlap with the lower rotational levels of a higher vibration state. Hence, the final term schema can be rather complex (see Fig. 2.8).

The energy distance between the electronic states is typically of the order of 10^5 K. In the case of H₂, the ground electronic state contains 14 vibrational states (Fig. 2.9.

2.3.1 Rotational lines

For simplicity, we consider here first diatomic molecules that we picture as rigid rotators. If we think of a diatomic molecule as a dumbbell oriented along the x-axis and fixed at its center of mass, it can rotate in two different planes, the (x,z)-plane and the (x,y)-plane. In classical mechanics, a dumbbell rotating about his axis through the center of mass has the possible energy states

$$E_{\rm rot} = \frac{J^2}{2I} \tag{2.27}$$

where I is the moment of inertia and J is the angular momentum. In quantum mechanics (without further derivation), this reads as

$$E_{\rm rot} = \frac{\bar{h}^2}{2I}J(J+1) = BJ(J+1)$$
(2.28)

where \bar{h} is the Planck constant $h/2\pi$ and J is now a dimensionless quantum number, called the rotational quantum number. It can only take integer values of $0, 1, 2, 3, \ldots$ We merge $h/(8\pi^2 I)$ into the



Figure 2.9: Potential energy of H_2 as a function of internuclear separation. The three solid curves correspond to the ground and first two excited electronic states. The horizontal lines represent vibrational energy levels. Arrows depict photo-excitation into the Lyman band, followed by either fluoresecence or dissociation (caption and figure from Stahler & Palla 2004).

rotational constant of a molecule B. It has the units of frequency or classically also cm⁻¹. Table 2.2 shows values of some representative molecules. I is the moment of inertia

$$I = \mu \langle r^2 \rangle \quad , \tag{2.29}$$

where r is the bond length and μ is the reduced mass of the molecule, here expressed for a diatomic molecule,

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{2.30}$$

Let us first consider diatomic linear molecules such as CO. Their rotational spectra are easily understood. A dipole radiative transition occurs for $\Delta J = 1$

$$\Delta E = Bh \left[J(J+1) - (J-1)J \right] = 2BhJ \quad . \tag{2.31}$$

Table 2.2: Molecular constants: reduced mass μ , rotational constant B, force constant k, dissociation energy E_{diss} .

| Molecule | B [GHz] | μ | $B [cm^{-1}]$ | internuclear distance [Å] | $k \; [{ m N/m}]$ | $E_{\rm diss} \ [eV]$ |
|----------------------------------|--------------------|------------------|------------------|---------------------------|-------------------|-----------------------|
| H_2 | 1824.2 | 0.504 | 60.85 | 0.741 | 5.2×10^2 | 4.478 |
| $^{12}C^{10}O$ $^{13}C^{16}O$ | $57.636 \\ 55.101$ | $6.856 \\ 7.172$ | $1.931 \\ 1.846$ | 1.128 1.128 | | 11.092 |
| SiO | 21.161 | 10.177 | 0.721 | 1.510 | | 8.26 |

The transitions $J \to J + 1$ are labelled as the R-branch, while the transitions $J \to J - 1$ are labelled the P-branch. The nomenclature here is $R(0)=0 \to 1$, $R(1)=1 \to 2$, etc. and the same holds for the P-branch starting with $P(1)=1 \to 0$. From these formulae, it is clear that the energy spacing is linear with J and the frequency separation is $\Delta \nu = 2B$. The lowest rotational transitions of CO are

$$J = 1 - 0 \qquad \lambda = 2.6 \text{ mm} \qquad \nu = 116 \text{ GhZ}$$
(2.32)

$$J = 2 - 1 \qquad \lambda = 1.3 \text{ mm} \qquad \nu = 232 \text{ GhZ}$$

$$J = 3 - 2 \qquad \lambda = 0.87 \text{ mm} \qquad \nu = 347 \text{ GhZ}$$

Once we go to higher rotational levels, the approximation of the rigid rotator becomes less good and there will occur deviations from centrifugal distortions.

The CO rotational lines are the brightest molecular rotational transitions from space. Thus they are frequently used in ground based observations of dense molecular environments. On a side note, if we measure the rotational spectrum very accurately, we can turn the exercise around and estimate the rotational constant B and hence the bond length from the spacing of the rotational lines.

2.3.2 Vibrational lines

The vibrational levels of a molecule lie at higher energies than the rotational levels. Fig. 2.10 illustrates the possible vibrational modes in the linear CO_2 molecule. We can consider the bonds between the atoms in the molecules as springs between the masses that allow them to move in one of the three vibrational modes: the symmetric stretching mode, the asymmetric stretching mode, and the bending mode. In the symmetric stretching mode, the carbon atom remains fixed while the two oxygen atoms move closer to and farther from the carbon atom. In the bending mode the central carbon atom moves up and down while the two outer oxygen atoms move up an down in the opposite direction. Finally, in the asymmetric stretch mode, all three atoms move left to right; one bond



The symmetric stretch mode

contracts while the other expands. Figure 2.10: Vibrational modes in the linear CO_2 If we solve the Schrödinger equation for a diatentic current for a diatentic current for the spacing of the vibrational energy levels

$$E(v) = h\nu_e(v + \frac{1}{2}) - \nu_e x_e(v + \frac{1}{2})^2 , \qquad (2.33)$$

where v is the vibrational quantum number (values of 0, 1, 2, ...) and ν_e is the fundamental frequency. Here, the first term corresponds to the harmonic oscillator approximation and the second term describes the anharmonic effect on the spring as it stretches. The fundamental difference to the rotational energy levels is that the ground vibrational state has a non-zero energy, namely $1/2h\nu_e$. The fundamental frequency is given by

$$\nu_e = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad , \tag{2.34}$$

where k is the force constant for the chemical bond, typically 500 N/m, and μ is again the reduced mass of the molecule. For vibrational transitions, selection rules are not as hard as for rotational transitions and so we observe various bands belonging to $\Delta v = \pm 1, \pm 2, \pm 3, \ldots$ However, the transitions become weaker with increasing change in vibrational quantum number.

To make things more complex, a vibrating molecule can rotate at the same time. Each vibrational level contains a ladder of rotational levels that will be populated according to the excitation conditions in which the molecule sits (often, but not necessarily local thermodynamic equilibrium). The spectrum is then a ro-vibrational spectrum, where during a transition the vibrational as well as the rotational quantum number can change.

Vibrational transitions of simple molecules such as CO, CO₂ and H₂O often lie in the infrared spectral range. There are two prominent windows accessible from Earth, $1 - 5 \mu m$ and $8 - 20 \mu m$.

2.3.3 Electronic transitions

The UV and visual spectroscopy of molecules corresponds to electronic transitions, that is electron rearrangements in the molecules. These are least constraining as they also change the strength of molecular bonds and can enable chemical reactions. An electronically excited molecule can become a reactive molecule.

Each electronic state has the full suite of vibrational states which is subsequently split up into the rotational ladder.

2.3.4 Local thermodynamic equilibrium

The strength of these molecular transitions depends on their transition probability, the Einstein A coefficient, and on the population of the involved levels. In general, allowed lines are stronger than forbidden lines, reflected in their large difference of Einstein A coefficients. The levels are populated and de-populated by collisions and line transitions.

In many environments, collisions dominate the population and de-population of levels and thus the level populations follow from the Boltzmann equation

$$\frac{n_i}{n_j} = \frac{g_i}{g_j} e^{-\Delta E/kT} \tag{2.35}$$

where n_i and n_j are the two level population numbers, g_i and g_j their respective statistical weights and ΔE the energy difference between them. Collisions are said to thermalize the level population numbers to the corresponding local temperature T of the gas.

Rotational level population numbers are often in LTE, because the energy spacing between them is small $(\Delta E \ll V)$ and so even at low temperatures collision partners carry enough energy to excite them. The statistical weight g_i of a rotational level is given by (2J+1). Since the energy spacing is linear, but the statistical weight increases with J. For a each temperature, level population numbers peak around a fixed rotational quantum number and this is reflected in the line strength of the associated P- and R-branches.

The critical density introduced above is a measure of the density at which the LTE approximation holds. If the particle density is larger than $n_{\rm crit}$, the level population numbers can be approximated using the Boltzmann equation and the local gas temperature. If $n < n_{\rm crit}$, the levels will be subthermally excited, meaning that the temperature derived from the level excitation temperature, $T_{\rm exc}$ — as derived from the population numbers — will be lower than the actual gas temperature, the kinetic temperature $T_{\rm kin}$.

2.3.5 Statistical equilibrium

If LTE is no longer a valid approximation, we need to calculate the level population numbers from the equations of statistical equilibrium, i.e. we consider all collisional and radiative processes that populate and de-populate a level n_i . Hence, we can study the temporal change of population for each level

$$\frac{dn_i}{dt} = \sum_{j>i} n_j \left(A_{ji} + B_{ji} P(\nu_{ji}) \right) + \sum_{j

$$-n_i \sum_{ji} B_{ij} P(\nu_{ij}) - n_i \sum_{j\neq i} n_j C_{ij} .$$$$

Here, the first three terms describe the population of level i through spontaneous and stimulated emission from higher levels, absorption from lower levels and collisions from all levels. The stimulated emission is described by the Einstein B coefficient, which is related through the expression

$$B_{ji} = \frac{c^2}{2h\nu^3} A_{ji}$$
(2.37)

to the Einstein A coefficient. The relation between the stimulated emission and the absorption coefficient B_{ij} is

$$g_i B_{ij} = g_j B_{ji} \tag{2.38}$$

The last three terms describe the de-population of level i via spontaneous and stimulated emission, absorption and collisions. Solving these equations requires a large amount of atomic/molecular data including accurate energy levels, transitions probabilities and collisional cross sections. Especially the latter are generally very difficult to find and often only crudely approximated. The accuracy of radiative transfer and line formation calculations depends largely on the level of accuracy of this atomic/molecular data.

2.3.6 Molecular line observations

We can use molecules as tracers of physical conditions, e.g. gas density and temperature. The amount of flux emitted in a particular line can be written as

$$F_x(\nu_{ji}) = N_j A_{ji} h \nu_{ji} \beta(\tau_{ji}) \Omega_{\text{source}} \quad , \tag{2.39}$$

where N_j is the column density of the molecule x being in the excited upper state j of the line transition with frequency ν_{ji} . β is the escape probability of that line photon and the value of β depends obviously on the optical depth of that particular line τ_{ji} . Ω_{source} is the solid angle of the source (e.g. the molecular cloud) on the sky. The difficulties in using molecular lines as physical tracers becomes immediately clear: we need to know the level population of the upper energy level — which requires often accurate knowledge of molecular collision cross sections — and we need to understand the optical depth effects, here simplified in form of the escape probability β . The last uncertainty is the abundance of the molecular species itself. However, in some cases, we can use simplifications that allow us to use certain molecular lines as density or temperature indicators.

One such example is the CO molecule. It is a very robust molecule that is only photodissociated at the skin of the cloud (Photon Dominated Regions - PDRs). Molecular chemistry (see later sections) locks at high extinction all carbon in the form of CO. Hence, in the interior of molecular clouds, we can approximate the CO abundance to be almost constant $\epsilon(CO) = 10^{-4}$. The only exception occurs at low temperatures T < 20 K, where CO can efficiently freeze out onto the cold dust grain surfaces. Since the molecule has very low critical densities for the low rotational transitions, we can assume LTE for the level populations of the rotational levels. To mitigate the problem of optical depth, we often use isotopes of CO which have up to a factor 1500 lower abundances.

Lines generally trace material in the density regime close to the critical density. The latter scales with ν^3 , i.e. J^3 for the rotational lines. Hence, higher rotational lines trace warmer and denser gas. If we choose the molecule (dipole moment) and the line transition (rotational quantum number J) well, we can probe gas in the entire temperature range between 10 and 1000 K and in the density range between 10^2 and 10^{10} cm⁻³. In the following, we give a few examples of specific lines and their diagnostic power.

Fig. 2.11 illustrates the entire parameter space of temperature and density and outlines the molecule and transition best used in each regime. The J=1-0, J=2-1 CO lines are good temperature indicators for densities $10^{2.5} < n(H_2) < 10^4 \text{ cm}^{-3}$. By using a combination of rotational lines, ranging from high to low optical depth, one can probe the physical conditions in the cloud as a function of depth. The highly optical thick lines of the main isotope originate close to the cloud surface, while the optically thin isotope lines probe down into the core of the molecular cloud.

At higher densities, NH_3 can be used instead of CO. The oscillation of the nitrogen atom through the hydrogen plane (Fig. 2.12) causes an inversion transition at microwave frequencies. The main line is at 1.27 cm. The right hand side of the figure shows NH_3 emission of the Ophiuchus F core. Stars denote locations of Class I protostars, while triangles indicate the positions of NH_3 clumps. There is good correspondence between the two.

At very low densities, typical for diffuse clouds, the hydroxyl radical, OH, can be used as a tracer. Its ground state hyperfine transitions lie around 18 cm and are thus easily seen in absorption against the background continuum emission. Its rotational levels have very high excitation temperatures and critical densities and are thus often detected in shocks.

2.4 Temperature structure

Molecular clouds consist of gas and dust with a typical mass ratio of 100. If the density and extinction are high, gas and dust temperature are well coupled through collisions and equal. Otherwise, both phases settle to their own equilibrium temperature.



Figure 2.11: Molecules as diagnostics as a function of gas temperature and density.



Figure 2.12: Left: inversion transition of NH_3 . Right: map of NH_3 emission towards the Ophiuchus star forming core, Oph F. Stars denote locations of Class I protostars, while triangles indicate the positions of NH_3 clumps (Friesen et al. 2009).

Dust radiative equilibrium



Figure 2.13: Energy balance for a dust grain.

2.4.1 Dust temperature

In the case of dust, the temperature is set by radiative equilibrium, i.e. the radiation energy absorbed by each dust grain Q_+ is re-emitted according to its temperature Q_- (Fig. 2.13). The timescale for reaching this equilibrium is generally short compared to the collisional energy exchange with the dust particles. In the optically thin case, we can write this balance as

$$Q_{+} = Q_{-} \qquad (2.40)$$
$$\pi a^{2} \int_{0}^{\infty} F_{\nu} \epsilon_{\nu} d\nu = 4\pi a^{2} \int_{0}^{\infty} \pi B_{\nu} (T_{\text{dust}}) \epsilon_{\nu} d\nu .$$

Here, a is the radius of the dust grain, ϵ_{ν} its frequency dependent absorption efficiency. We have assumed here, that the grains radiate as black bodies and thus absorption and emission efficiencies are equal and we can use the Planck function to characterize the emitted spectrum of the dust grain. F_{ν} is the external radiation field that the grain 'sees'. For certain grain size limits, we can solve this equation analytically. For that, we assume that the external radiation field can be characterized through a black body of temperature T_* . For large grains, the opacity is grey and we can write

$$T_{\rm dust} = \sqrt{\frac{R_*}{2r}} T_* \quad . \tag{2.41}$$

This equation can for example be used in approximating the temperatures of planets in our Solar System. In the limit of micron-sized dust grains, the opacity is high ($\epsilon = 1$) at short wavelength (compared to the size of the grains) and follows a power law $1/\lambda$ at long wavelengths. Hence, we obtain

$$T_{\rm dust} = 324 \left(\frac{L_*}{L_{\odot}}\right)^{0.2} \left(\frac{a}{\mu \rm m}\right)^{-0.2} \left(\frac{r}{\rm AU}\right)^{-0.4} .$$
(2.42)

We use here the unit AU for the distance to the radiation source, because this formula is most useful in the context of debris disks. In molecular clouds, dust grains are typically much smaller than micron sized. And there, we have to solve the dust radiative equilibrium numerically. In addition, we have to take into account optical depth effects.

2.4.2 Gas temperature

Just as for the dust, the gas temperature can be found from the equilibrium between heating and cooling processes

$$\sum_{i} \Gamma_{i} = \sum_{j} \Lambda_{j} \quad , \tag{2.43}$$

where the complication arises from the fact that there is not a single heating mechanisms or cooling mechanism, but a series of processes. Depending on the particular physical and chemical environment, we may be lucky to identify *the* most important heating and *the* most important cooling process and thus solve the formula analytically. But in most cases, we cannot identify a single process and even if, the process itself is often intimately coupled to the chemical structure of the cloud through the abundances of certain molecules.

Heating processes

Heating of the cloud occurs through cosmic rays and radiation. Cosmic rays consist of relativistic protons and a mixture of heavy elements such as iron and electrons. Cosmic rays span an enormous range in energies between 10 and 10^{14} MeV. They originate in supernova explosions.

A cosmic ray that travels into a molecular cloud interacts with the nuclei and electrons of the elements there. The excitation of the nuclei decays through emission of γ -rays that escape the cloud. The electronic excitation leads to dissociation, ionization, and emission of UV photons. The most likely process is ionization of molecular hydrogen — which is often the most abundant species inside the molecular clouds —

$$p^+ + H_2 \rightarrow H_2^+ + e^- + p^+$$
 (2.44)

The ejected electron carries a large amount of kinetic energy, typically 30 eV, and can cause secondary ionization of molecular hydrogen as well as collisional excitation. The latter process is heating the gas. The heating rate per unit volume can be written as

$$\Gamma_{\rm CR}({\rm H}_2) = \zeta({\rm H}_2) n_{\rm H_2} \Delta E({\rm H}_2) \quad . \tag{2.45}$$

Here, $\zeta(H_2)$ is the ionization rate of molecular hydrogen. The amount of heat released per ionization is $\Delta E(H_2) = 7.0$ eV. The reason for ΔE being smaller than the typical 30 eV is in fact the secondary ionization. We can write down a similar formula for neutral hydrogen using $\zeta(HI)$ and $\Delta E(HI) = 6.0$ eV.

The dominant heating process at the surface of molecular clouds is photoelectric heating (Fig. 2.14). UV radiation hitting a dust grain ejects an electron which transmits its kinetic energy to the gas through subsequent collisions. The typical work function of a neutral grain is $W \sim$ 6 eV. The liberated photoelectron has a certain probability to leave the grain and must also overcome the charge potential of the grain (in case it is not neutral). Typical electron energies are of the order of 1 eV. The efficiency of ejecting a photoelectron for each incoming photon is close to one for very small grains. Only in grains that are larger than the typical mean free path of the electron inside the grain, this efficiency drops significantly.



Figure 2.14: Photoelectric effect on interstellar and circumstellar dust grains.

The reason for this is that the photoelectron has a higher probability to be re-absorbed inside the grain. We can write the heating rate as

$$\Gamma_{\rm PE} = 4\pi n_{\rm dust} \sigma_{\rm dust} \epsilon_{\rm PE} \int_0^{\nu_{\rm W}} J_\nu d\nu \quad , \tag{2.46}$$

where n_{dust} and σ_{dust} are the dust grain number density and the grain surface area. ϵ_{PE} is the efficiency of ejecting a photoelectron. The interstellar radiation field is integrated down to the frequency ν_{W} , which is the threshold frequency corresponding to the work function W.

Cooling processes

Most of the cooling in molecular clouds is due to collisional ionization of atoms or molecules and subsequent radiation of a photon that escapes the cloud. One of the most efficient molecules in the cooling of molecular clouds is CO through its rotational lines. At the surface of clouds, where molecules are photodissociated, most of the cooling is due to fine structure lines of neutral oxygen and ionized carbon, [O I] 63 and 145 μ m and [C II] 157 μ m.

Dust grains can also cool the gas if the dust temperature is lower than that of the gas. In that case, collisions between gas particles and dust grains lead to an exchange of energy which does not affect the dust radiative equilibrium (see note above on the timescale of dust radiative equilibrium)

$$\Lambda_{\rm gas-grain} = \frac{3}{2} k_B \left(T_{\rm gas} - T_{\rm dust} \right) \frac{n_{\rm dust}}{t_{\rm coll}} \ . \tag{2.47}$$

Here, k_B is the Boltzmann constant and t_{coll} is the collision timescale. We see from this formula that the rate turns into a heating rate if $T_{\text{dust}} > T_{\text{gas}}$.

2.4.3 Cloud temperatures

We see from the above processes of heating and cooling that most heating rates scale linearly with density, while cooling processes scale quadratic in density (at least under LTE conditions where collisions dominate the level population). Hence, denser environments will be colder, i.e. the molecular clouds are cooler than diffuse clouds.

At the surface of the molecular clouds, molecules are efficiently photodissociated and the ambient radiation field can easily penetrate up to an extinction of $A_V \sim 1$. This surface is often called a photon dominated region (PDR). The MC surface is mostly atomic consisting of atomic hydrogen, neutral oxygen and ionized carbon. Most metals with a low ionization energy such as carbon, silicon, magnesium, iron etc. are efficiently ionized by the interstellar radiation field. Hydrogen and oxygen have higher ionization potentials of 13.60 and 13.62 eV. Thus at the surface of the cloud, the most relevant heating process is photoelectric heating while cooling proceeds through the [C II] fine structure line at 157 μ m. We can thus approximate the gas temperature by equating those two processes

$$\Gamma_{\rm PE} = \Lambda_{\rm C\,II} \quad , \tag{2.48}$$

yielding an approximate expression for the gas temperature at the surface

$$T_{\rm gas} = \frac{40 \text{ K}}{2.0 + \log \left(n_{\rm H} / 10^3 \text{ cm}^{-3} \right)} \quad . \tag{2.49}$$

Deep inside molecular clouds, cosmic ray heating is the only remaining heating process — photons cannot reach here due to the high extinction. The cooling is predominantly by CO rotational lines. We can thus find the gas temperature from

$$\Gamma_{\rm CR} = \Lambda_{\rm COrot} \quad . \tag{2.50}$$

Typical gas temperatures are of the order of 10 K. Fig. 2.15 illustrates the typical temperature profile derived for a molecular cloud.

2.5 Chemistry

Just as level populations can be approximated through LTE (local thermodynamic equilibrium) or SE (statistical equilibrium), chemistry can assume various equilibria.

The most constraining one is thermodynamic equilibrium in which each reaction is counterbalanced by its own backreaction, leading to the concept of equilibrium constants K describing these as a function of temperature

$$K = \frac{k_{\text{forward}}}{k_{\text{backward}}} \quad . \tag{2.51}$$

These constants depend only on temperature and this type of equilibrium is typically found in very dense environments such as stellar atmospheres, planetary atmospheres and the densest inner regions of protoplanetary disks.



Figure 2.15: Temperature profiles in the lower density region of a molecular cloud. The solid curve represents the gas temperature, while the dashed line refers to dust grains. The lower dotted curve results from balancing cosmic-ray heating and CO cooling in the gas (figure and caption from Stahler & Palla 2004.

The alternative is stationary chemistry, which assumes that the density of each species reaches a stationary value, i.e. does not change with time. For gas phase chemistry, this can be described with a rate equation approach, where the time variation in the average density of a species is given by the sum of various production and loss rates. A generic rate equation for species i is

$$\frac{dn_i}{dt} = P_i - L_i$$
(2.52)
$$= \sum_{jl} k_{ijl}(T_g) n_j n_l + \sum_j \left(\Gamma_{ij}(r, z) + \zeta_{ij}(r, z) \right) - n_i \left[\sum_{jl} k_{jil}(T_g) n_l + \sum_j \left(\Gamma_{ji}(r, z) + \zeta_{ji}(r, z) \right) \right],$$

where n_i is the average volume density of species i and P_i and L_i are the chemical production and loss rates for that species. The first and third sums are the production and loss terms for species i through chemical reactions with species j and l, at rates k_{ijl} and k_{jil} . The second and fourth sums are the production and loss terms for species i through photoreactions involving species j (at rates Γ_{ij} and Γ_{ji}) and cosmic ray reactions involving species j (at rates ζ_{ij} and ζ_{ji}).

On the other hand, grain surface chemistry is stochastic in nature and strongly depends on the surface coverage of the species involved in the reaction at any instant. Hence, it is much better described using a master equation approach instead of a rate equation,

$$\frac{d}{dt}P(i_1\dots i_N) = \sum (\text{accretion} + \text{evaporation} + \text{surface reactions})$$

where P is the probability that i particles of species 1 to N are on the grain surface. Caselli et al. (1998) and Caselli et al. (2002) find that the rate equation approach can be modified for grain surface chemistry by taking into account the accretion timescale for a species as well as its migration timescale on the grain surface. This enables efficient simultaneous treatment of gas- and dust-phase chemistry.

Under some astrophysical conditions — low densities, low temperatures — , chemical equilibrium is hardly reached on timescales of $10^5 - 10^6$ yr. This is especially relevant for diffuse and molecular clouds. In that case, we have to solve the time-dependent rate equations.

2.5.1The formation of molecules

Under typical molecular cloud conditions (temperature and density), chemistry proceeds through two body interaction. If we first consider the collision of two atoms. The formation of a molecule requires the excess energy needs to be either transmitted to a third body or radiated away. A third collision partner is not an option given the low density of interstellar space. An exception is the formation of molecular hydrogen on grain surfaces, where the grain acts as the third body. Alternatively, a photon can carry away the excess energy in a reaction type called radiative association. Here, the molecule is formed in an excited state that decays radiatively to the ground state. However, the most important type of reaction in interstellar chemistry is ion-molecule reactions

$$A^+ + B \to C^+ + D$$
 . (2.53)

The rate coefficient for such reactions is of the order of $k \sim 10^{-9} \text{ cm}^3/\text{s}$ and depends only weakly on temperature. The reason for the large rate coefficient is that the charged particle induces a dipole moment in the neutral one, thereby enhancing the cross section of the reaction over the geometric one (Coulomb interaction). The counterbalancing process is often dissociative recombination with free electrons

$$A^+ + e^- \to B + C \quad . \tag{2.54}$$

The electron recombines with the positive molecule creating an excited unstable neutral molecule. In most cases, the molecule autoionizes and returns the electron to the gas phase. However, if the constituents separate before autoionization occurs, the molecule dissociates into two neutral species. The typical rate coefficient is of the order of 10^{-7} cm³/s for temperatures around 100 K and increases slowly with decreasing temperature.

2.5.2 Chemical networks

In order to understand molecule formation, we need to take into account all possible reactions among all possible species. Given the shear amount of atoms and molecules, this sounds like a hopeless endeavor. However, there exist large molecular databases that contain collections of molecular reactions that can occur under interstellar densities and temperatures. One of them is the UMIST database.

Selecting a number of atoms and molecules — based on abundance and experience — and using such a database allows us to build a chemical reaction network that interconnects all those species through chemical reactions. We can then solve for the abundances of all species using either a stationary approximation $dn_i/dt = 0$ or the time-dependant approach.

In this way, we find for example that under the typical conditions of dense cores, all carbon is turned into CO on timescales of 10^6 yr.

2.5.3 Chemical structure of molecular clouds

The surface of a molecular cloud resembles a PDR and shows the typical H/H_2 and $C^+/C/CO$ transition with increasing A_V (Fig. 2.16). The location where hydrogen turns molecular can be simply found from the equilibrium between H_2 formation on grain surfaces and H_2 photodissociation by interstellar UV photons

$$R_{\text{form}} n(\mathbf{H}) n_{\mathbf{H}} = \zeta(N_{\mathbf{H}_2}) n(\mathbf{H}_2)$$
 . (2.55)

The photodissociation process of H₂ proceeds via discrete bands. Once these H₂ bands become optically thick, photodissociation is largely suppressed by self-shielding. Hence, the photodissociation rate ζ depends to first order on the column density of H₂, N_{H₂}. Assuming now that the total hydrogen number density is $n_{\rm H} = n({\rm H}) + 2n({\rm H_2})$, we can work out the molecular fraction as a function of column density into the cloud

$$\frac{n({\rm H}_2)}{n({\rm H})} = \frac{R_{\rm form} n_{\rm H}}{2R_{\rm form} n_{\rm H} + \zeta(N_{\rm H_2})} \quad .$$
(2.56)

The ionization degree inside the molecular cloud is low, because CR are the only remaining ionization source via the following processes



Figure 2.16: A schematic diagram of a photodissociation region (PDR). The PDR is illuminated from the left and extends from the predominantly atomic surface region to the point where O_2 is not appreciably photodissociated ($A_V \sim 10$ visual magnitude). Hence, the PDR includes gas whose hydrogen is mainly H₂ and whose carbon is mostly CO. Large columns of warm O, C, C⁺, and CO and vibrationally excited H₂ are produced in the PDR. The gas temperature T_{gas} generally exceeds the dust temperature T_{dust} in the surface layer. Figure and caption taken from Hollenbach & Tielens (1997).

$$H_2 + CR \rightarrow H_2^+ + e^-$$
 (2.57)

$$H_2 + CR \rightarrow H^+ + H + e^-$$
 (2.58)

$$He + CR \rightarrow He^+ + e^-$$
 (2.59)

The secondary electrons are energetic and cause additional ionization and also excitation of molecular hydrogen. When H₂ decays to the ground state, secondary UV photons are generated that can cause additional ionization deep inside the cloud. Dust grains can act as a sink of electrons and become negatively charged. Typical electron densities in the cloud interior are of the order of $10^{-7} n_{\rm H}$.