

Chapter 5. Molecular Spectroscopy: Basic Physics

Notes:

- *Most of the material presented in this chapter is taken from Stahler and Palla (2004), Chap. 5.*

5.1 Interstellar Molecules

The first thing that needs to be explained when considering the existence of interstellar molecules is the fact that they are there at all. Indeed, the presence of ultraviolet photons in the interstellar radiation field would lead us to believe that any molecules previously created would be destroyed by these high-energy photons. In the present day Universe, the solution to this problem resides in the fact that wherever we find molecular gas, we also find interstellar dust. We know that dust grains are extremely efficient in absorbing radiation at optical and ultraviolet wavelengths, and, therefore, provide the amount of shielding necessary to protect molecules against harmful radiation.

Another problem consists in explaining how atoms can combine to form both simple and more complicated molecules. One might assume that normal neutral-neutral interaction in the gas phase of the interstellar medium would suffice to explain the current observations of the many different molecular species detected so far (well over 100) in the dense and cold parts of molecular clouds. As it turns out, there are a few reasons that render this hypothesis unlikely. First, it is often the case that an energetic **activation barrier** needs to be conquered before a neutral-neutral chemical reaction can take place. Since the corresponding energy level is on the order of $\Delta E/k_B \sim 100$ K, this type of reaction is unlikely to take place in such regions of molecular clouds.

Another problem arises from the fact that most chemical reactions are **exothermic**, i.e., they liberate energy upon the creation of a molecule. This characteristic, combined with the requirement that energy and momentum be conserved during a chemical reaction, makes it impossible for a two-body interaction to take place. Technically, there is still the possibility that the molecule resulting from a two-body interaction would be initially in an excited state and subsequently emit a photon, which would make possible such a chemical reaction while ensuring that the aforementioned conservation laws are met. This process known as **radiative association** is, however, very unlikely to take place in molecular clouds. It appears that the only way out for the existence of this kind of reaction resides with the presence of a third body, which would then easily ensure the conservation of momentum and energy. But such three-body interactions (between three hydrogen atoms, for example) would require much higher densities than encountered in the dense and cold parts of molecular clouds. We must, therefore, also discard this possibility as the main pathway for molecule production (although we will see later that we cannot completely neglect them).

We now consider another factor that enters the equation when one calculates the rate at which any chemical reaction, of any kind, between two particles can take place. Although we have just dismissed the possibility of neutral-neutral reactions as a viable explanation for the existence of the many molecular species detected in dense molecular clouds, we do this calculation for comparison purposes at a later time. Let us take, for example, two

neutral species A and B that coexist in some region of a cloud with respective densities n_A and n_B . Let us now calculate the **collision rate** of a given particle B collides with another A such that the following reaction could, in principle, take place



where C is the molecule that results from this interaction. If σ is the scattering cross-section characterizing the collision, then the volume covered or traveled by the particle B as seen by A per unit time is $|v_r|\sigma$, where v_r is the relative velocity between the two. It follows that the probability that the particle B meets any particle A is

$$v_c = n_A |v_r| \sigma, \quad (5.2)$$

which is, in effect, the collision rate for this type of encounter. If we assume equipartition of energy, the relative velocity between two particles in a gas of temperature T is approximately

$$v_r \approx \left(\frac{k_B T}{\mu} \right)^{1/2}, \quad (5.3)$$

where μ is the reduced mass for the two particles considered. For a typical molecular cloud with $T = 10$ K, the relative velocity is on the order of 0.1 km/s. Also, the cross-section σ for neutral atoms or molecules collisions is approximately 10^{-15} cm². We, therefore, find from equation (5.2) that the collision rate is

$$v_c \approx 10^{-11} n_A \text{ s}^{-1}, \quad (5.4)$$

and n_c the total number of collisions per unit volume and unit time is

$$n_c \approx 10^{-11} n_A n_B \text{ cm}^{-3} \text{ s}^{-1}. \quad (5.5)$$

Furthermore, if the **reaction rate coefficient** is denoted by k (in cm³s⁻¹), then the average number of reactions taking place per unit time is

$$N_r = k n_A n_B \text{ s}^{-1}. \quad (5.6)$$

Comparison with equation (5.2) reveals that the reaction rate coefficient already incorporates the collision rate within it. We note for the moment that the value obtained in equation (5.4) for the collision rate leading to neutral-neutral reactions is a function of the relative velocity between the two particles involved. One could always postulate that, for some reason, the relative velocity is increased by a large factor (e.g., an order of magnitude or two), if this were needed to explain observations. A problem with this scenario is that it would be very hard for two particles colliding at such high speeds to

“stick” together and enter into a chemical reaction. They would most likely bounce off each other instead.

It was eventually discovered that the way out of the problem of accounting for the observed population of molecular species in dense molecular clouds is to involve charged atoms or molecules in chemical reactions. These are called **ion-molecule reactions**. This is due to the fact that when an ion approaches a neutral particle it will induce an electric dipole moment into that neutral entity that will greatly increase the scattering cross-section. More precisely, it can be shown that

$$\sigma \propto v_r^{-1}, \quad (5.7)$$

and that the mean collision rate of any ion A^+ with a neutral B leading to a potential reaction of the type



is

$$v_c = n_A \langle v_r \sigma \rangle. \quad (5.9)$$

The difference with a neutral-neutral collision is quantified by the fact that

$$\langle v_r \sigma \rangle \approx 10^{-9} \text{ cm}^3 \text{ s}^{-1}, \quad (5.10)$$

which is the equivalent of a neutral-neutral collision with a relative velocity of 10 km/s (see equation (5.4))! For similar volume densities as for a neutral-neutral interaction, the collision rates are increased by two orders of magnitudes. Furthermore, ion-molecule reactions do not involve any activation barrier, in general. These facts are sufficient to account for the molecular abundances measured in molecular clouds, at least generally speaking.

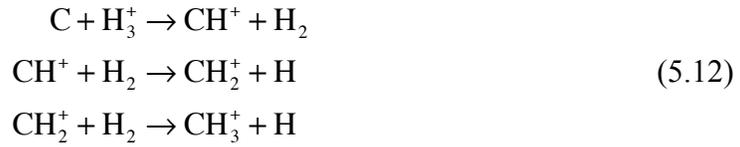
We should note that a certain level of ionization, if very low (i.e., 10^{-6} to 10^{-9}), is always expected to be present in molecular clouds, even in cases where there are no stellar or interstellar radiation fields in the vicinity. This is because of the omnipresence of cosmic rays that can penetrate deep into molecular clouds to bring about some level of ionization.

Perhaps the most fundamental ion-molecule reaction is

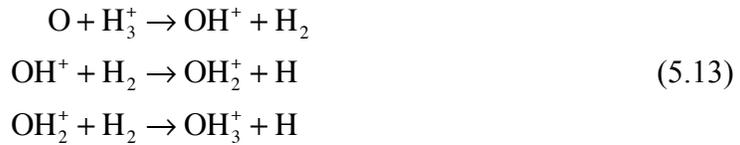


The importance of this reaction stems from the high chemical reactivity of the H_3^+ ion and its ensuing role for the formation of many other molecules. For example, we can show how the combination of this reactivity with the existence of atomic carbon and oxygen, which are produced abundantly in stellar interiors and injected in the interstellar

medium at the end of their lives, leads to the formation of carbon monoxide (CO). More precisely, we have



for part of the so-called carbon chemistry, and a similar network



for the oxygen chemistry. Combining the last reaction of these networks with O and C, respectively, yields the formation of the very important HCO^+ molecular ion



Finally, since most of the resulting ions will be destructed through **dissociative recombination** with an electron e^- we get



Carbon monoxide is very stable molecule (it has a triple-bond between the two atom) and is the second most abundant molecule after molecular hydrogen.

Evidently our main reaction given in equation (5.11) assumes the presence of molecular hydrogen. As it turns out, this is not a trivial assumption. This is because the chemical reaction involving two hydrogen atoms to form a hydrogen molecule is exothermic (see above). As was mentioned earlier, because of the need for conservations of energy and momentum in the process of creating the molecule the energy released in the creation of the molecule must be transmitted to a third body. A solution to this problem can be found if one considers the role played by dust grains for the formation of molecules, especially H_2 .

Because a hydrogen atom has an unpaired electron it will easily stick (through the weak Van der Waals force) to the surface of a grain after a collision with it. It will then quantum tunnel through the surface of the grain until it reaches a lattice defect where the binding energy is high enough to trap it in place. Evidently, the probability that two atoms meet at the location of such a defect on the surface of grain and form a molecule can be relatively high if enough atoms collide with the dust grain. It is, in fact, believed that two atoms will quickly find each other in such a way at the surface of a grain. If the collision rate of a grain with hydrogen atoms is given by (see equation (5.2))

$$v_c = n_H |v_r| \sigma_d, \quad (5.16)$$

where $\sigma_d = \pi a_d^2$ is the cross-section of a (spherical) dust grain and n_H the density of atomic hydrogen. Then the rate of H_2 formation is given by

$$\begin{aligned} \mathcal{R}_{H_2} &= \frac{1}{2} \gamma_H n_d v_c \\ &= \frac{1}{2} \gamma_H n_d n_H |v_r| \sigma_d, \end{aligned} \quad (5.17)$$

where $\gamma_H \approx 0.3$ is the sticking probability of a hydrogen atom to the surface of the grain. The factor of $1/2$ in equation (5.17) is due to the fact that two atoms are needed to create one molecule. Once the molecule has formed the energy release in the process is easily absorbed by the dust grain, which is much more massive than the atoms, and the molecule is ejected from the surface of the grain. Moreover, since they ejected hydrogen molecules do not have any unpaired electron (unlike the hydrogen atom) they will not exhibit the tendency to easily stick to a dust grain when colliding at a later time. Dust grains are thus essential for the formation of the most abundant molecule in molecular clouds, and allow for the creation of the H_3^+ molecule (through the reaction given in equation (5.11)) that is so important for the chemistry and the formation of many other molecules.

5.2 Molecular Spectroscopy

Molecules being composed of nuclei and electrons along with their interwoven interactions are, needless to say, impossible systems to completely solve analytically. It follows that a series of approximations are usually applied when trying to explore their spectroscopy.

We start with the **classical molecular Hamiltonian**, which is the sum of the kinetic and potential energies

$$\begin{aligned} T &= \frac{1}{2} \sum_{r=1}^l m_r (\dot{X}_r^2 + \dot{Y}_r^2 + \dot{Z}_r^2) \\ V &= \sum_{r<s=1}^l \frac{C_r C_s e^2}{R_{rs}}, \end{aligned} \quad (5.18)$$

where, for the r^{th} particle, m_r is the mass, the position is specified by $X_r, Y_r,$ and Z_r and measured from some arbitrary space-fixed coordinate system, $C_r e$ is the charge, and R_{rs}

$$R_{rs} = \sqrt{(X_r - X_s)^2 + (Y_r - Y_s)^2 + (Z_r - Z_s)^2} \quad (5.19)$$

is the distance to particle s . The kinetic energy can be decomposed into two components: one (T_{CM}) due to the motion of the centre of mass of the system, and another (T_{rve}) arising from the motions of the nuclei and electrons relative to the centre of mass. To separate these two terms, we express X_r, Y_r , and Z_r the position components of the r^{th} particle relative to the centre of mass located at X_0, Y_0 , and Z_0 such that

$$\begin{aligned} X_r &= X_r + X_0 \\ Y_r &= Y_r + Y_0 \\ Z_r &= Z_r + Z_0. \end{aligned} \quad (5.20)$$

Once the ensuing calculations are performed we find the following for the Hamiltonian

$$\begin{aligned} H_{\text{rve}} &= T_{\text{rve}} + V \\ &= \frac{1}{2} \sum_{r=2}^l m_r (\dot{X}_r^2 + \dot{Y}_r^2 + \dot{Z}_r^2) + \frac{1}{2m_1} \sum_{r,s=2}^l m_r m_s (\dot{X}_r \dot{X}_s + \dot{Y}_r \dot{Y}_s + \dot{Z}_r \dot{Z}_s) \\ &\quad + \sum_{r<s=1}^l \frac{C_r C_s e^2}{R_{rs}}, \end{aligned} \quad (5.21)$$

The index “rve” stands for **rovibronic** (rotation-vibration-electronic), and is associated with the *internal* kinetic energy of the molecule, as opposed to the *external* or translational kinetic energy. The rovibronic Hamiltonian is the quantity that we need to consider to determine the spectroscopy of a molecule.

To convert the classical rovibronic Hamiltonian H_{rve} into the needed quantum mechanical version of the Hamiltonian, we must first express equation (5.21) as a function of the coordinates X_r, Y_r , and Z_r and momenta P_{X_r}, P_{Y_r} , and P_{Z_r} . We could then replace these quantities with the corresponding quantum mechanical operators and obtain an expression for the quantum mechanical Hamiltonian. To accomplish our first aforementioned task, we make use of the Lagrangian definition for the momenta, i.e.,

$$P_{X_r} = \frac{\partial L_{\text{rve}}}{\partial \dot{X}_r}, \dots, \quad (5.22)$$

where $L_{\text{rve}} \equiv T_{\text{rve}} - V$ is the (rovibronic) Lagrangian. In this case, since the potential energy is not a function of the velocities, then equation (5.22) simplifies to

$$P_{X_r} = \frac{\partial T_{\text{rve}}}{\partial \dot{X}_r}, \quad (5.23)$$

and so on. The equation resulting from this is

$$\hat{H}_{\text{rve}} = -\hbar^2 \sum_{r=2}^l \frac{1}{2m_r} \nabla_r^2 + \frac{\hbar^2}{2M} \sum_{r,s=2}^l \nabla_r \cdot \nabla_s + \sum_{r<s=1}^l \frac{C_r C_s e^2}{R_{rs}}, \quad (5.24)$$

with

$$\nabla_r = \mathbf{e}_x \frac{\partial}{\partial X_r} + \mathbf{e}_y \frac{\partial}{\partial Y_r} + \mathbf{e}_z \frac{\partial}{\partial Z_r}, \quad (5.25)$$

as a representation in the usual coordinate space.

5.2.1 The Fine Structure and Hyperfine Structure Hamiltonians

The rovibronic Hamiltonian of equation (5.24) does not take into account some interactions due to the intrinsic magnetic moment (i.e., spin) of the electrons, and the intrinsic magnetic and electric moments of the nuclei. More precisely, if we only consider the individual electron spins $\hat{\mathbf{s}}_i$, and the so-called electron *spin-spin* and *spin-orbit* couplings, then the **electron fine structure Hamiltonian** \hat{H}_{es} must be introduced

$$\begin{aligned} \hat{H}_{\text{es}} \simeq & -\left(\frac{e}{m_e c}\right)^2 \sum_{j \neq i} \frac{1}{R_{ij}^3} \left[(\hat{\mathbf{R}}_i - \hat{\mathbf{R}}_j) \times \left(\frac{\hat{\mathbf{P}}_i}{2} - \hat{\mathbf{P}}_j \right) \right] \cdot \hat{\mathbf{s}}_i \\ & + \frac{e}{m_e c^2} \sum_{\alpha, i} \frac{C_\alpha e}{R_{i\alpha}^3} \left[(\hat{\mathbf{R}}_i - \hat{\mathbf{R}}_\alpha) \times \left(\frac{\hat{\mathbf{P}}_i}{2m_e} - \frac{\hat{\mathbf{P}}_\alpha}{m_\alpha} \right) \right] \cdot \hat{\mathbf{s}}_i \\ & + \left(\frac{e}{m_e c}\right)^2 \sum_{j>i} \left[\frac{1}{R_{ij}^3} (\hat{\mathbf{s}}_i \cdot \hat{\mathbf{s}}_j - \frac{3}{R_{ij}^2} [\hat{\mathbf{s}}_i \cdot (\hat{\mathbf{R}}_i - \hat{\mathbf{R}}_j)] [\hat{\mathbf{s}}_j \cdot (\hat{\mathbf{R}}_i - \hat{\mathbf{R}}_j)]) \right. \\ & \left. - \frac{8\pi}{3} \delta(\hat{\mathbf{R}}_i - \hat{\mathbf{R}}_j) (\hat{\mathbf{s}}_i \cdot \hat{\mathbf{s}}_j) \right], \end{aligned} \quad (5.26)$$

where α labels the nuclei, and i and j label the electrons. In equation (5.26), the first term (a spin-orbit interaction) corresponds to the coupling of the spin of each electron to the magnetic field it feels (in its reference frame) because of the presence of the electric Coulomb fields due to the other electrons (in their respective reference frames). The second term is also a spin-orbit interaction but this time with the Coulomb field of the nuclei, and the last term corresponds the spin-spin couplings between the intrinsic magnetic moments of each pair of electrons. The internal molecular Hamiltonian then becomes $\hat{H}_{\text{int}} = \hat{H}_{\text{rve}} + \hat{H}_{\text{es}}$, and the total angular momentum must include both the orbital and electron spin momenta. It is usual to denote the orbital angular momentum with $\hat{\mathbf{N}}$ (instead of $\hat{\mathbf{J}}$), and the total angular momentum with $\hat{\mathbf{J}}$. We then write

$$\hat{\mathbf{J}} = \hat{\mathbf{N}} + \hat{\mathbf{S}}, \quad (5.27)$$

where $\hat{\mathbf{S}}$ is the total electron spin operator. The associated quantum numbers J and m refer to the sum of the orbital and spin angular momenta, and are those with which the molecular eigenfunctions can be labeled.

On the other hand, if the interactions of the intrinsic magnetic and electric moments of the nuclei are taken into account, then the total angular momentum is denoted by $\hat{\mathbf{F}}$ with

$$\hat{\mathbf{F}} = \hat{\mathbf{J}} + \hat{\mathbf{I}} = \hat{\mathbf{N}} + \hat{\mathbf{S}} + \hat{\mathbf{I}}, \quad (5.28)$$

where $\hat{\mathbf{I}}$ is the total nuclear spin angular momentum. The corresponding **nuclear hyperfine structure Hamiltonian** \hat{H}_{hfs} will include nuclei spin interactions similar in form to those of equation (5.26), as well as terms due to the nuclei electric quadrupole fields. The internal molecular Hamiltonian then becomes

$$\hat{H}_{\text{int}} = \hat{H}_{\text{rve}} + \hat{H}_{\text{es}} + \hat{H}_{\text{hfs}}, \quad (5.29)$$

and the good quantum numbers with which the associated eigenfunctions can be labeled are those corresponding to \hat{F}^2 and \hat{F}_Z , i.e., F and m_F ($|m_F| = 0, 1, 2, \dots, F$).

5.2.2 The Born-Oppenheimer Approximation

Coming back to equation (5.24) for the rovibronic Hamiltonian, we can simplify things greatly with the realization that the motion of the electrons can be separated from that of the nuclei. This is expected because of the significantly lower mass of the electrons. We can therefore imagine that as the nuclei are moving around, the electron will adjust themselves on a much shorter time scale (almost instantaneously as far as the nuclei are concerned). This is the idea at the centre of the so-called **Born-Oppenheimer approximation**.

To proceed with this approximation, we introduce a new coordinate system that has its origin at the *nuclear* centre of mass instead of the molecular centre of mass. This difference in the location of the origin is important as it relates the motion of the electrons to the position of the nuclei. The Hamiltonian then becomes

$$\hat{H}_{\text{rve}} = \hat{T}_{\text{e}} + \hat{T}_{\text{N}} + V(\mathbf{R}_{\text{N}}, \mathbf{r}_{\text{e}}), \quad (5.30)$$

where \hat{T}_{e} and \hat{T}_{N} are the separated kinetic energies of the electrons and nuclei, respectively. The potential energy can also be advantageously written as

$$V(\mathbf{R}_{\text{N}}, \mathbf{r}_{\text{e}}) = V_{\text{ee}}(\mathbf{r}_{\text{e}}) + V_{\text{NN}}(\mathbf{R}_{\text{N}}) + V_{\text{Ne}}(\mathbf{R}_{\text{N}}, \mathbf{r}_{\text{e}}), \quad (5.31)$$

where the different terms on the right hand side are for the separate summations of electron-electron, nucleus-nucleus, and nucleus-electron electrostatic potential energies, respectively. This Born-Oppenheimer approximation also implies that it is possible to

express the rovibronic wave function $\Phi_{rve,nj}^0$ as the product of the electronic wave function $\Phi_{elec,n}$ and the rotation-vibration wave function $\Phi_{rv,nj}$

$$\Phi_{rve,nj}^0 = \Phi_{elec,n}(\mathbf{R}_N, \mathbf{r}_e) \Phi_{rv,nj}(\mathbf{R}_N), \quad (5.32)$$

where the indices n and j relate to the particular electronic and rotation-vibration states, respectively. Obviously, we must realize that although the nuclei coordinates \mathbf{R}_N are assumed constant in $\Phi_{elec,n}$, they are certainly allowed to vary in $\Phi_{rv,nj}$. The Schrödinger equation is then

$$\begin{aligned} \hat{H}_{rve} \Phi_{rve,nj}^0(\mathbf{R}_N, \mathbf{r}_e) &= \left[(\hat{T}_e + V_{ee} + V_{Ne}) + (\hat{T}_N + V_{NN}) \right] \Phi_{elec,n}(\mathbf{R}_N, \mathbf{r}_e) \Phi_{rv,nj}(\mathbf{R}_N) \\ &= (\hat{T}_e + V_{ee} + V_{Ne}) \Phi_{elec,n}(\mathbf{R}_N, \mathbf{r}_e) \Phi_{rv,nj}(\mathbf{R}_N) \\ &\quad + \Phi_{elec,n}(\mathbf{R}_N, \mathbf{r}_e) (\hat{T}_N + V_{NN}) \Phi_{rv,nj}(\mathbf{R}_N) \\ &= V_{elec,n} \Phi_{elec,n}(\mathbf{R}_N, \mathbf{r}_e) \Phi_{rv,nj}(\mathbf{R}_N) \\ &\quad + \Phi_{elec,n}(\mathbf{R}_N, \mathbf{r}_e) (\hat{T}_N + V_{NN}) \Phi_{rv,nj}(\mathbf{R}_N) \\ &= \Phi_{elec,n}(\mathbf{R}_N, \mathbf{r}_e) (\hat{T}_N + V_{NN} + V_{elec,n}) \Phi_{rv,nj}(\mathbf{R}_N), \end{aligned} \quad (5.33)$$

or

$$\begin{aligned} \hat{H}_{rve} \Phi_{rve,nj}^0(\mathbf{R}_N, \mathbf{r}_e) &= E_{rve,nj}^0 \Phi_{elec,n}(\mathbf{R}_N, \mathbf{r}_e) \Phi_{rv,nj}(\mathbf{R}_N) \\ &= E_{rve,nj}^0 \Phi_{rve,nj}^0(\mathbf{R}_N, \mathbf{r}_e), \end{aligned} \quad (5.34)$$

with $E_{rve,nj}^0$ the eigenvalue when the molecule is in the electronic state n and rotation-vibration state j . It is therefore apparent that the potential energy for the nuclear rotation-vibration Hamiltonian is $(V_{NN} + V_{elec,n})$ and includes a contribution from the electronic state through the presence of $V_{elec,n}$. It is customary to rewrite things so that the *zero energy* for the rotation-vibration equation, in a given electronic state, is the minimum value of $(V_{NN} + V_{elec,n})$, which is usually called the *electronic energy* $E_{elec,n}$. Our molecular problem can then be rewritten with two Schrödinger equations: one determining the electronic states and another the nuclear (rotation-vibration) states

$$\begin{aligned} (\hat{T}_e + V_{ee} + V_{Ne}) \Phi_{elec,n}(\mathbf{R}_N, \mathbf{r}_e) &= V_{elec,n} \Phi_{elec,n}(\mathbf{R}_N, \mathbf{r}_e) \\ (\hat{T}_N + V_{NN}) \Phi_{rv,nj}(\mathbf{R}_N) &= E_{rv,nj} \Phi_{rv,nj}(\mathbf{R}_N), \end{aligned} \quad (5.35)$$

with

$$\begin{aligned}
V_{N,n} &= V_{\text{NN}} + V_{\text{elec},n} - E_{\text{elec},n} \\
E_{\text{rv},nj} &= E_{\text{rve},nj}^0 - E_{\text{elec},n}.
\end{aligned}
\tag{5.36}$$

5.2.3 Separation of Vibration and Rotation Motions

A further simplification of the problem is effected by introducing yet another coordinate system. This new system also has its origin at the nuclear centre of mass, but it is fixed to nuclei in such a way as to follow the rotational motion of the molecule. In comparison, the coordinate systems considered until now have been fixed in “space”.

Once this substitution is made in the rotation-vibration Hamiltonian, and many other approximations are made (e.g., ignoring terms due to Coriolis interactions, anharmonic vibrational motions, etc.), it is possible to separate the two types of motion. The resulting Hamiltonian corresponding to the second of equations (5.35) is

$$\hat{H}_{\text{rv}}^0 = \frac{1}{2} \sum_{\alpha} \mu_{\alpha\alpha}^e \hat{J}_{\alpha}^2 + \frac{1}{2} \sum_{k=1}^{3N-6} (\hat{P}_k^2 + \lambda_k Q_k^2),
\tag{5.37}$$

where $\mu_{\alpha\alpha}^e$ are the reciprocal of the principal moments of inertia of the molecule, \hat{J}_{α} are the components of the total angular momentum, and Q_k , λ_k , and \hat{P}_k are, respectively, the normal modes of vibrations, their eigenvalues, and their associated linear momenta.

A solution to the vibration part of the Hamiltonian (that of a harmonic oscillator)

$$\hat{H}_{\text{vib}}^0 = \frac{1}{2} \sum_{k=1}^{3N-6} (\hat{P}_k^2 + \lambda_k Q_k^2),
\tag{5.38}$$

yields a set of wave functions $\Phi_v(Q)$, which depend on the normal modes of vibration (one for each non-degenerate mode or set of degenerate modes), with associated energy levels that are functions of the vibrational quantum number v . For a non-degenerate mode the energy levels are given by

$$E_{\text{vib}} = \left(v + \frac{1}{2} \right) \hbar^2 \gamma,
\tag{5.39}$$

where $v = 0, 1, 2, \dots$ and $\gamma \equiv \lambda^{1/2}/\hbar$. The total energy of vibration for a molecule will consist of the summation over all the energies (of the type given by equation (5.39)) over all normal modes of vibration.

The rotational Hamiltonian (that of a rigid rotator) is usually written

$$\begin{aligned}
\hat{H}_{\text{rot}}^0 &= \frac{1}{2} \sum_{\alpha} \mu_{\alpha\alpha}^e \hat{J}_{\alpha}^2 \\
&= A_e \hat{J}_a^2 + B_e \hat{J}_b^2 + C_e \hat{J}_c^2,
\end{aligned}
\tag{5.40}$$

where

$$A_e = \frac{1}{2I_{aa}^e}, \quad B_e = \frac{1}{2I_{bb}^e}, \quad \text{and} \quad C_e = \frac{1}{2I_{cc}^e}. \quad (5.41)$$

The principal axes a, b , and c are always defined such that $A_e \geq B_e \geq C_e$, and whether the molecular fixed z -axis (fixed to the nuclei of the molecule when not vibrating) is identified with the a, b , and c index the situation is usually defined as type I, II, or III.

The quantity B_e is the **rotational constant**.

It is convenient to discern between the following types of rotators

1. Spherical tops		$I_{aa}^e = I_{bb}^e = I_{cc}^e$	CH_4
2. Symmetric tops,	a) prolate	$I_{aa}^e < I_{bb}^e = I_{cc}^e$	CH_3D
	b) oblate	$I_{aa}^e = I_{bb}^e < I_{cc}^e$	$\text{H}_3^+, \text{NH}_3$
3. Linear molecules		$I_{aa}^e = 0, I_{bb}^e = I_{cc}^e$	CO, HCN
4. Asymmetric tops		$I_{aa}^e < I_{bb}^e < I_{cc}^e$	H_2O

The solution to Schrödinger equation for the Hamiltonian of equation (5.40) will differ depending on what type of molecule is being considered. Examples of configuration for the rotational energy levels for molecules of the different types (i.e., spherical top, symmetrical top, linear, and asymmetric top molecules) are shown in Figure 5.1. For the purpose of our discussion it will be sufficient to limit ourselves to the case of linear molecules, it is then easy to show that the solution can be written as

$$B_e \hat{J}^2 \Phi_J(\varphi, \theta, \chi) = E_{\text{rot}} \Phi_J(\varphi, \theta, \chi), \quad (5.42)$$

and

$$E_{\text{rot}} = B_e J(J+1) \hbar^2, \quad (5.43)$$

where $\Phi_J(\varphi, \theta, \chi)$ is the wave function associated to the angular momentum quantum number J . The quantities φ, θ , and χ are the Euler angles that relate the position of the molecule-fixed and space-fixed set of axes at all times.

Finally, referring to equations (5.35), (5.39), and (5.40) we find that the total energy of a molecule (within our set of approximations) can be written as

$$\begin{aligned} E_{\text{rv},nj} &= E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}} \\ &= E_{\text{elec},n} + \left(v + \frac{1}{2} \right) \hbar^2 \gamma + B_e J(J+1) \hbar^2. \end{aligned} \quad (5.44)$$

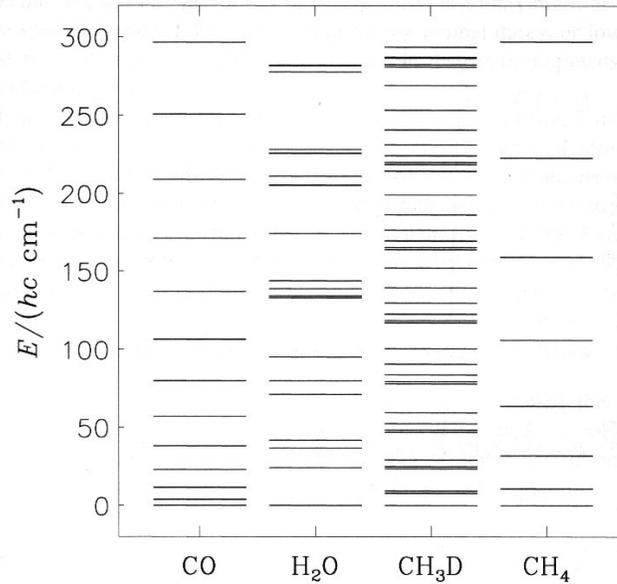


Figure 5.1 - Rotational energy levels for molecules of the different types (i.e., spherical top (CH_4), symmetric top (CH_3D), linear (CO), and asymmetric top (H_2O) molecules).

It is also important to note that these energies scale in such a way that

$$E_{\text{elec}} \gg E_{\text{vib}} \gg E_{\text{rot}}. \quad (5.45)$$

It follows that the gas in the dense and cold parts of molecular clouds will mainly radiate through rotational transitions. The other types of transitions will happen in hotter regions, such as regions located close to protostars or within shock fronts.

5.2.4 Selection Rules

Whenever a molecule possesses a finite **electric dipole moment** $\hat{\mu}$, it will regulate its interaction with any ambient electric field. More precisely, to adequately account for this interaction the molecular Hamiltonian must be augmented by the following perturbation term

$$\hat{H}_{\text{dip}} = -\hat{\mu} \cdot \mathbf{E}, \quad (5.46)$$

The electric dipole is defined as

$$\hat{\mu} = \sum_i C_i e \hat{\mathbf{R}}_i, \quad (5.47)$$

where $C_i e$ and $\hat{\mathbf{R}}_i$ are the charge and the space-fixed position of particle i , respectively (the summation is over all electrons and nuclei).

Selection rules for transitions within the Born-Oppenheimer, harmonic oscillator, and rigid rotators approximations can be established by a careful quantum mechanical analysis that specifies which states (i.e., wave functions) will be coupled by the perturbation Hamiltonian of equation (5.46). There is no simple way to state what electronic transitions will be allowed or not. Fortunately, such rules can be established for vibrational, rotational, and rovibrational transitions for the different types of molecules (i.e., rotators).

In general, vibrational transitions for a given normal mode (of index ν_r) are unrestricted. That is,

$$\Delta\nu_r = \nu_r' - \nu_r'' = \pm 1, \pm 2, \pm 3, \dots, \quad (5.48)$$

where ν_r' and ν_r'' are the initial and final states, respectively. However, the so-called **infrared active** transitions (they happen in the infrared) with $\Delta\nu_r = \pm 1$ will normally be stronger. Other types of transitions, such as **overtone** (from the vibrational ground state to one state r with $|\Delta\nu_r| \geq 2$) and **combination tones** (from the vibrational ground state to more than one state r with $|\Delta\nu_r| \neq 0$) transitions are also possible.

Rotational transitions, whether pure (i.e., $\Delta\nu_r = 0$ and no change in electronic state) or combined with vibrational transitions, are more complicated to generalize. But a rule on the angular momentum quantum number J can be stated with

$$\Delta J = J' - J'' = 0, \pm 1 \quad (J' = J'' = 0 \text{ is forbidden}). \quad (5.49)$$

where J' and J'' are the initial and final states, respectively. The reader should be aware, however, that the simplicity of the rule given in equation (5.49) is somewhat misleading, as other quantum numbers come into play for rotational transitions. Furthermore, these vary with the type of rigid rotator considered. In particular, **pure rotational transitions** (i.e., $\Delta\nu_r = 0$ and no change in electronic state) for symmetric top and linear molecules are only allowed when

$$\Delta J = \pm 1 \quad (5.50)$$

because of energy and angular momentum conservations considerations. A transition with $\Delta J = 0$ will only be allowed if $\Delta\nu_r \neq 0$, as long as $J' = J'' \neq 0$; these are **rovibrational transitions**.

A molecule will have no electric dipole whenever it is symmetric (e.g., H_2 , H_3^+ , and CH_4 in their electronic ground states). In such cases, interaction of the molecule with an ambient electric field will be regulated through its **electric quadrupole moment** $\hat{Q}_{\alpha\beta}$ (it is a second rank tensor) through the corresponding perturbation Hamiltonian

$$\hat{H}_{\text{quad}} = -\frac{1}{6} \sum_{\alpha,\beta} \hat{Q}_{\alpha\beta} \frac{\partial E_{\alpha}}{\partial x_{\beta}}. \quad (5.51)$$

The electric quadrupole moment is defined as

$$\hat{Q}_{\alpha\beta} = \sum_i C_i e \left(3\hat{X}_{\alpha,i} \hat{X}_{\beta,i} - \hat{R}_i^2 \delta_{\alpha\beta} \right), \quad (5.52)$$

where $C_i e$, $\hat{X}_{\alpha,i}$, and \hat{R}_i are the charge, and the α th component and the modulus of the space-fixed position of particle i , respectively (the summation is over all electrons and nuclei). The main difference in the selection rules, as compared to electric dipole transitions, is restricted to the rotational transitions. More precisely, we find that

$$\Delta J = J' - J'' = 0, \pm 1, \pm 2 \quad (J' = J'' = 0 \text{ is forbidden}), \quad (5.53)$$

where J' and J'' are the initial and final states, respectively. The other rules and comments described earlier for the electric dipole interaction also apply for the electric quadrupole transitions. However, it should always be kept in mind that other considerations can restrict these selection rules (e.g., conservation of energy and momenta, and Pauli's exclusion principle).

5.3 The Hydrogen Molecule

It is rather ironic that perhaps the two most important molecules in molecular clouds, i.e., H_2 and H_3^+ , are symmetric. It follows that they cannot be detected through the strong electric dipole transitions (they do not possess a dipole), but can only be observed via the relatively weaker electric quadrupole counterparts. Furthermore, this fact, combined with the low temperatures characterizing the dense and cold parts of molecular clouds, implies that these molecules will not be detectable in these regions (i.e., the quadrupole transitions will be too weak). Astronomers rely instead on other molecular species as tracers for these molecules (e.g., CO for H_2). On the other hand, H_2 and H_3^+ can be observed in other types of environment (e.g., shocks), which are energetic enough to induce electronic and vibrational transitions.

Molecular hydrogen will then be subjected to the selection rules specified by equations (5.48) and (5.53) with the additional restrictions imposed on the nuclear spin states by the Pauli exclusion principle. This is because the two nuclei are identical particles (i.e., protons), and their associated spin wave functions will impose certain symmetries on the rovibrational wave functions to allow for quadrupole radiative transitions. More precisely, the selection rules for the angular momentum quantum number is not given by equation (5.53) but

$$\Delta J = J' - J'' = 0, \pm 2 \quad (J' = J'' = 0 \text{ is forbidden}). \quad (5.54)$$

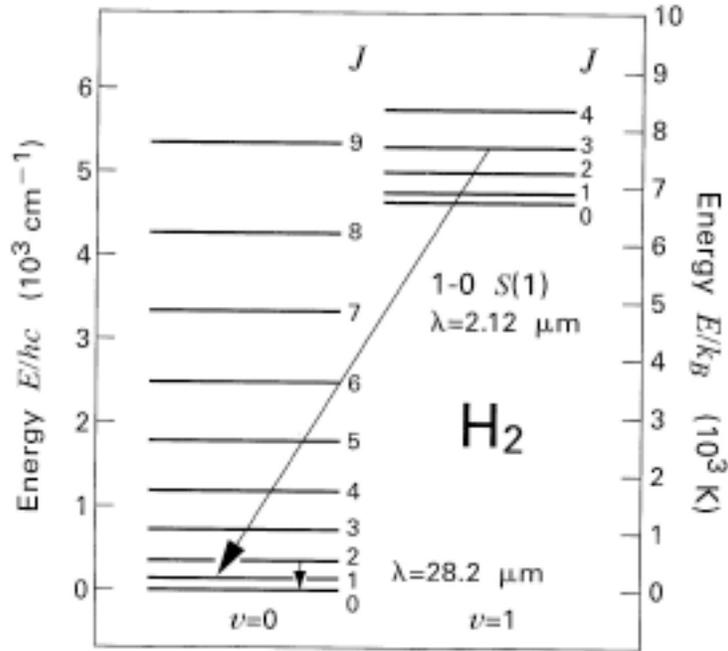


Figure 5.2 – Rotational levels of H_2 for the first two vibrational states. The $J = 2 \rightarrow 0$ pure rotational electric quadrupole transition in the vibrational ground state is shown, as well as the $1-0 S(1)$ rovibrational transition.

Since H_2 is the molecule with the smallest moment of inertia, the energy spacing between its rotational transitions will be the greatest (see equations (5.40) to (5.43)). For example, the $J = 2 \rightarrow 0$ pure rotational electric quadrupole transition in the vibrational ground state has an energy $h\nu/k_B = 510 \text{ K}$, which is too high for cold molecular clouds. It is customary to denote a general rovibrational transition between the initial and final states (ν', J') and (ν'', J'') with $\nu' - \nu'' = O(J''), Q(J''), S(J'')$, depending whether $\Delta J = 2, 0$, or -2 , respectively. For example, the well-known $1-0 S(1)$ transition that occurs at $2.12 \mu\text{m}$ is shown in Figure 5.2. As can also be seen from this figure, the energy separation between vibrational states is on the order of almost 10^4 K . The corresponding separation for electronic states is even higher at approximately 10^5 K .

5.4 Carbon Monoxide

Carbon monoxide is not symmetric and, therefore, has a finite electric dipole moment that allows for the detection of strong pure rotational transitions with $\Delta J = \pm 1$ (see equation (5.50)). Furthermore, this molecule also has a sizeable principle moment of inertia about axes perpendicular to the molecular axis. This implies that the spacing between adjacent energy levels will be accordingly small. Indeed, the energy associated with the fundamental $J = 1 \rightarrow 0$ ($\nu = 0$) pure rotational transition is $\Delta E_{10}/k_B = 5.5 \text{ K}$; this transition occurs at a wavelength of 2.6 mm or a frequency of 115 GHz . The next transition $J = 2 \rightarrow 1$ at 230 GHz has a corresponding energy of 16 K . We have here a molecule that lends itself perfectly to the observational study of the cold regions of

molecular clouds. The $J = 1 \rightarrow 0$ transition, as well as the positions of rotational energy levels, is shown in Figure 5.1.

5.4.1 The Critical Density

Molecules located deep inside molecular clouds, away from any substantial sources of radiation, will be excited through collisions with mainly H_2 . How much a given CO rotational level, in this case, will be populated depends on the number of, and the energy involved in, collisions. Referring to equations (5.2) and (5.3) for the neutral-neutral collision rate we realize that the level of excitation will depend on both the density of H_2 and the **kinetic temperature** T_{kin} of the gas.

We define the **critical density** of the gas n_{crit} for a well-defined transition the density at which, for a given temperature T_{kin} , the collision rate is equal to the **Einstein coefficient for spontaneous emission** A_{ul} between the upper (u) and lower (l) levels defining the transition. That is, there must be enough collisions to maintain a consistent population for the upper level of the transition. For example, for the $J = 1 \rightarrow 0$ transition of CO at $T_{kin} = 10$ K we have $A_{10} = 7.5 \times 10^{-8} \text{ s}^{-1}$. Equating the collision rate given by equation (5.4) to this coefficient yields $n_{H_2} \approx 7.5 \times 10^3 \text{ cm}^{-3}$. A more careful evaluation of the collision rate for these conditions would yield the more correct value of $n_{H_2} = 3 \times 10^3 \text{ cm}^{-3}$.

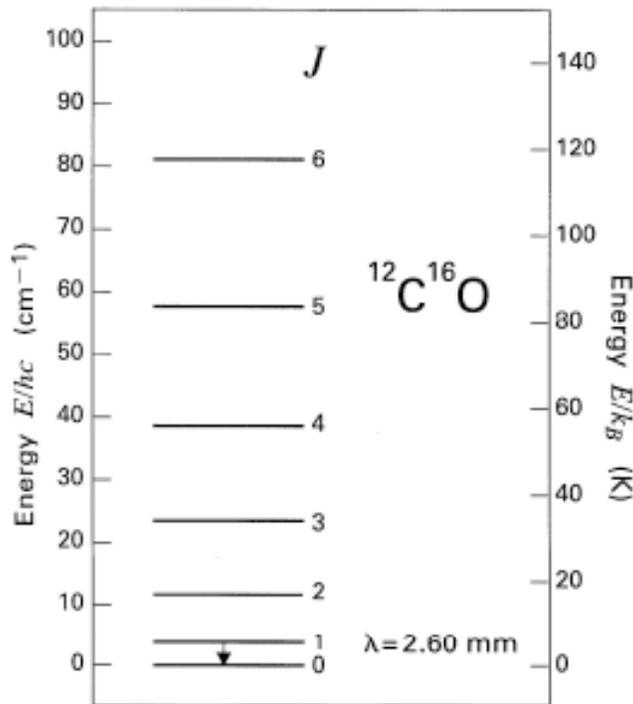


Figure 5.3 – Pure rotational transitions of carbon monoxide within the ground vibrational state $v = 0$.

As the density of the gas increases beyond the critical density for the $J = 1 \rightarrow 0$, other levels lying at higher energies will also become significantly populated as long as the density reaches their associated critical densities. The populations of the different levels are then given by **Boltzmann's relation**

$$\frac{N_j}{g_j} = \frac{N_{\text{tot}}}{U(T_{\text{ex}})} e^{-E_j/k_{\text{B}}T_{\text{ex}}}, \quad (5.55)$$

where N_j is the number of molecules in the state of energy E_j and degeneracy g_j , N_{tot} is the total number of molecules, and $U(T_{\text{ex}})$ is the partition function at the excitation temperature T_{ex} . When the levels are all populated through collisions as is assumed here, then $T_{\text{ex}} = T_{\text{kin}}$ and the molecules are in **local thermodynamic equilibrium** (LTE).

5.4.2 Vibrational transitions

In regions that are hot enough (e.g., in the surroundings of young stars) vibrational transitions such as those discussed in Section 5.2.4 can arise, and will generally be accompanied with rotational transitions (hence rovibrational transitions). For these it is possible that $\Delta J = 0, \pm 1$. Depending on the value of ΔJ , we have the **P-branch** ($\Delta J = -1$), the **Q-branch** ($\Delta J = 0$), and the **R-branch** ($\Delta J = 1$).