Chapter Five

Energy Levels of Molecules

This chapter reviews the energy-level structure of small molecules, with particular attention to selected molecules of astrophysical interest: H_2, CO, OH, NH_3, and H_2O. Just as for Chapter 4, Chapter 5 should be regarded as reference material – give it a quick once-over now, then return to it when you need to understand observations of some molecule.

5.1 Diatomic Molecules

It is helpful to consider first the hypothetical case where the nuclei are fixed, and only the electrons are free to move – this is known as the **Born-Oppenheimer approximation**. In atoms and atomic ions, the electrons move in a spherically symmetric potential, and the total electronic orbital angular momentum L_e is a good quantum number. In molecules, the electrons move in a Coulomb potential due to two or more nuclei, and spherical symmetry does not apply. However, in the case of diatomic molecules (or, more generally, linear molecules), the Coulomb potential due to the nuclei is symmetric under rotation around the nuclear axis (the line passing through the two nuclei), and L_{ez} =(the projection of the electronic angular momentum onto the internuclear axis)$/\hbar$ is a good quantum number. It is conventional to define $\Lambda \equiv |L_{ez}|$. Because the potential is axially symmetric, the two states $L_{ez} = \pm\Lambda$ have the same energy.

5.1.1 Fine-Structure Splitting

In addition, S_{ez} =(projection of the total electron spin onto the internuclear axis)$/\hbar$ is also a good quantum number; define $\Sigma \equiv |S_{ez}|$.

J_{ez} =(projection of the total electronic angular momentum on the internuclear axis)$/\hbar$ is also a good quantum number. If Λ and Σ are both nonzero, then there are two possible values: $J_{ez} = |\Lambda - \Sigma|$ and $J_{ez} = \Lambda + \Sigma$.

States with different $|J_{ez}|$ will differ in energy due to fine-structure splitting.

5.1.2 Hyperfine Splitting

If one or more nuclei have nonzero nuclear spin *and* $J_{ez} \neq 0$, then there will be an interaction between the nuclear magnetic moment and the magnetic field generated

by the electrons, resulting in "hyperfine splitting": the energy will depend on the orientation of the nuclear angular momentum (or angular momenta) relative to the axis. As in atoms, this splitting is small, of order $\sim 10^{-6}$ eV.

5.1.3 Designation of Energy Levels: Term Symbols

Diatomic molecules with identical nuclei (e.g., H_2, N_2, O_2) are referred to as **homonuclear**. Note that the nuclei must be truly *identical* – HD and $^{16}O^{17}O$ are not homonuclear molecules. The energy levels of homonuclear diatomic molecules are designated by **term symbols**

$$^{(2\Sigma+1)}\mathcal{L}_{u,g} \ ,$$

where

$\mathcal{L} = \Sigma, \Pi, \Delta, ...$ for $\Lambda = 0, 1, 2, ...$, where $\Lambda\hbar$ = projection of the electron orbital angular momentum onto the internuclear axis,

$\Sigma\hbar$ = projection of the electron spin angular momentum onto the internuclear axis.

$$u, g = \begin{cases} g & (\text{"gerade"}) \text{ if symmetric under reflection through the} \\ & \quad \text{center of mass,} \\ u & (\text{"ungerade"}) \text{ if antisymmetric under reflection through the} \\ & \quad \text{center of mass.} \end{cases}$$

For the special case of Σ states, a superscript + or – is added to the term symbol:

$$^{(2\Sigma+1)}\Sigma^{\pm}_{u,g} \ ,$$

where the superscript

$$\pm = \begin{cases} + & \text{if symmetric under reflection through (all) planes} \\ & \quad \text{containing the nuclei,} \\ - & \text{if antisymmetric under reflection through a plane} \\ & \quad \text{containing the nuclei.} \end{cases}$$

In the case of a **heteronuclear** diatomic molecule (e.g., HD, OH, or CO), the energy levels are designated

$$^{(2\Sigma+1)}\mathcal{L}_{J_{e,z}}$$

where $\mathcal{L}$ and Σ have the same meaning as for homonuclear diatomic molecules, but now $J_{e,z}$ is indicated as a subscript. As for homonuclear molecules, if the term symbol is Σ, then an additional superscript $\pm$ is applied, specifying the symmetry of the wave function under reflection through planes containing the nuclei.

Because a given molecule may have more than one electronic state with the same term symbol, the electronic states are distinguished by a letter X, A, B, ..., a, b, ...

Table 5.1 Selected Diatomic Molecules[a]

	Ground term	B_0/hc [b] (cm^{-1})	B_0/k [b] (K)	r_0 [d] (Å)	μ [c] (D)	ν_0/c [b] (cm^{-1})	Λ-doubling
H_2	$^1\Sigma_g^+$	59.335[f]	85.37	0.741	0	4161	–
CH	$^2\Pi_{1/2,3/2}$	14.190	20.42	1.120[g]	1.406[g]	2733.	$\nu \approx 3.3\,\mathrm{GHz}$
CH^+	$^1\Sigma_0^+$	13.931	20.04	1.131	1.679[e]	2612.	–
OH	$^2\Pi_{3/2,1/2}$	18.550	26.69	0.9697	1.6676	3570.	$\nu \approx 1.61\,\mathrm{GHz}$
CN	$^2\Sigma_{1/2}^+$	1.8910	2.721	1.1718	0.557[i]	2042.	–
CO	$^1\Sigma_0^+$	1.9225	2.766	1.1283	0.1098	2170.	–
SiO	$^1\Sigma_0^+$	0.7242	1.042	1.5097	3.098	1230.	–
CS	$^1\Sigma_0^+$	0.8171	1.175	1.5349	2.001[h]	1272.	–

[a] Data from Huber & Herzberg (1979) unless otherwise noted.
[b] $E(v, J) \approx h\nu_0(v + \frac{1}{2}) + B_0 J(J + 1)$ [see Eq. (5.2)].
[c] μ = permanent electric dipole moment.   [g] Kalemos et al. (1999).
[d] r_0 = internuclear separation.   [h] Maroulis et al. (2000).
[e] Folomeg et al. (1987).   [i] Neogrády et al. (2002).
[f] Jennings et al. (1984).

appearing in front of the term symbol. The letter X is customarily used to designate the electronic ground state. The ground terms for a number of diatomic molecules of astrophysical interest are given in Table 5.1, along with the internuclear separation r_0 and the electric dipole moment μ.

5.1.4 O, P, Q, R, and S Transitions

A diatomic molecule can vibrate (stretch) along the internuclear axis, and it can rotate around an axis perpendicular to the internuclear axis. The rotational angular momentum adds (vectorially) to the electronic angular momentum.

The rotational levels of diatomic molecules are specified by a single vibrational quantum number v and rotational quantum number J. Transitions will change J by either 0, ± 1, or ± 2. It is customary to identify transitions by specifying the upper and lower electronic states, upper and lower vibrational states, and one of the following: $O(J_\ell)$, $P(J_\ell)$, $Q(J_\ell)$, $R(J_\ell)$, $S(J_\ell)$, where the usage is given in Table 5.2. Thus, for example, a transition from the $v_\ell = 0$, $J_\ell = 1$ level of the ground electronic state to the $v_u = 5$, $J_u = 2$ level of the first electronic excited state would be written B–X 5–0 $R(1)$.

Table 5.2 Usage of O, P, Q, R, and S

Designation	$(J_u - J_\ell)$	Note
$O(J_\ell)$	-2	Electric quadrupole transition
$P(J_\ell)$	-1	Electric dipole transition
$Q(J_\ell)$	0	Electric dipole or electric quadrupole; $Q(0)$ is forbidden
$R(J_\ell)$	$+1$	Electric dipole transition
$S(J_\ell)$	$+2$	Electric quadrupole transition

5.1.5 H_2

The electronic ground state of H_2 (two electrons) has zero electronic orbital angular momentum ($L_e = 0$), has zero electron spin ($S_e = 0$), is symmetric under reflection through the center of mass (g), and is symmetric under reflection through planes containing the nuclei (+). The ground state is X $^1\Sigma_g^+$.

Consider the two nuclei at some fixed separation r_n: one can solve the electron Schrödinger equation for the electrons moving in this potential and obtain the electron eigenfunctions ψ_q and eigenenergies $E_q^{(e)}(r_n)$, where q denotes the quantum numbers that characterize the eigenfunction. If we (slowly) vary the internuclear separation r_n, the electron eigenfunctions ψ_q will change adiabatically, as will the eigenenergies $E_q^{(e)}(r_n)$. Therefore, we can define a function

$$V_q(r_n) \equiv E_q^{(e)}(r_n) + Z_1 Z_2 \frac{e^2}{r_n} \tag{5.1}$$

that is an effective potential governing the internuclear separation. In Figure 5.1, we show the effective internuclear potential $V_q(r_n)$ for the electronic ground state and the first two excited states of H_2.

If we consider only radial, or "vibrational," motions of the two nuclei, the internuclear separation obeys an equation of motion identical to that of a particle with a mass equal to the "reduced mass" $m_r = m_1 m_2/(m_1 + m_2)$, moving in a potential $V_q(r)$. The vibrational energy levels are quantized, with vibrational quantum number $v = 0, 1, 2, ...$ corresponding to the number of nodes in the vibrational wave function. Suppose that $V_q(r)$ has a minimum at nuclear separation r_0. In the neighborhood of r_0, the potential can be approximated $V_q(r) \approx V_q(r_0) + (1/2)k(r-r_0)^2$, corresponding to a "spring constant" k characterizing the curvature of the potential. Classically, for small-amplitude vibrations we would have a harmonic oscillator with angular frequency $\omega_0 = (k/m_r)^{1/2}$. The spring constant $k = d^2V_q/dr^2$ is closely related to the strength of the chemical bond. While k will differ from one chemical bond to another, it varies less than does the reduced mass. Hydrides (i.e., species of chemical formula XH) will have the smallest reduced mass, with H_2 being the extreme limit, with $m_r = m_H/2$. Therefore, the H_2 molecule has an unusually high fundamental vibrational frequency ω_0, corresponding to a wavelength $\lambda \approx 2.1\,\mu m$.

In addition to vibrational motion, the two nuclei can also undergo rotational motion around their center of mass, with quantized angular momentum $J\hbar$, where $J = 0, 1, 2, ...$ Classically, the rotational kinetic energy of a rigid rotor is $(J\hbar)^2/2I$, where I is the moment of inertia of the molecule. If we consider masses m_1 and m_2 separated by distance r_0, the moment of inertia $I = m_r r_0^2$. Quantum-mechanically, we replace the classical J^2 by $J(J+1)$. Therefore, we expect the rotational kinetic energy $E_{rot} = J(J+1)\hbar^2/2m_r r_0^2$, and the total vibration-rotation energy when in

electronic state q is, in the harmonic-oscillator and rigid-rotor approximation:

$$E_q(v, J) = V_q(r_0) + h\nu_0 \left(v + \frac{1}{2} \right) + B_v J(J+1) \quad , \tag{5.2}$$

$$\nu_0 \equiv \frac{\omega_0}{2\pi} \qquad B_v = \frac{\hbar^2}{2m_r r_0^2} \quad . \tag{5.3}$$

The $1/2$ in the $(v+1/2)$ term corresponds to the "zero-point energy" – the quantum vibrator cannot be localized at the potential minimum, and the lowest vibrational level corresponds to an energy $(1/2)\hbar\omega_0$ above $V_q(r_0)$. The constant B_v is referred to as the "rotation constant"; the subscript v is because the moment of inertia depends on the vibrational state. Pure vibrational transitions $v \to v-1$ have energy $h\nu_0$. Pure rotational transitions $J \to J-1$ have energy $h\nu = 2B_v J$

Equation (5.2) is not exact. The potential $V(r)$ is not quadratic, so that the vibrations are not exactly harmonic. In addition, the molecule is not a rigid rotor: the moment of inertia I depends on the state of vibration and also on the state of rotation (in high J states, the molecule gets stretched, resulting in a larger moment of inertia). Note also that r_0 and k depend on which electronic state the molecule
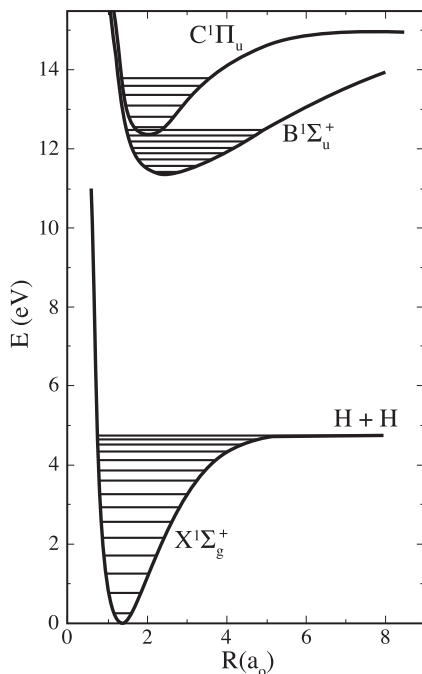

Figure 5.1 Effective internuclear potential for H_2 for the ground state $X^1\Sigma_g^+$ and the first two electronic excited states, $B^1\Sigma_u^+$ and $C^1\Pi_u$

is in: the excited electronic states will have different values of ω_0 and B_v than the ground state.

Each electronic state q therefore supports a vibration–rotation spectrum of energy levels, with energies $E_q(v, J)$. In Figure 5.2, we show the vibration–rotation levels of the ground electronic state of H_2.

5.1.6 Ortho-H_2 and Para-H_2

In the case of H_2, the electronic wave function is required to be antisymmetric under exchange of the two electrons. The two protons, just like the electrons, are identical fermions, and therefore the Pauli exclusion principle antisymmetry requirement also applies to exchange of the two protons. The protons are spin 1/2 particles – the two protons together can have total spin 1 (spins parallel) or total spin 0 (spins antiparallel). Without going into the quantum mechanics, the consequence of the antisymmetry requirement is that if the protons have spin 0, the rotational quantum number J must be even; this is referred to as **para-H_2**, with $J = 0$, 2, 4, ... If the two protons are parallel, with total spin 1, the rotational quantum number J must be odd: this is referred to as **ortho-H_2**, with $J = 1$, 3, 5, ... Because the nuclear spins are only weakly coupled to the electromagnetic field, ortho-H_2 and para-H_2 behave as almost distinct species, with conversion of ortho to para, or para to ortho, happening only very slowly.
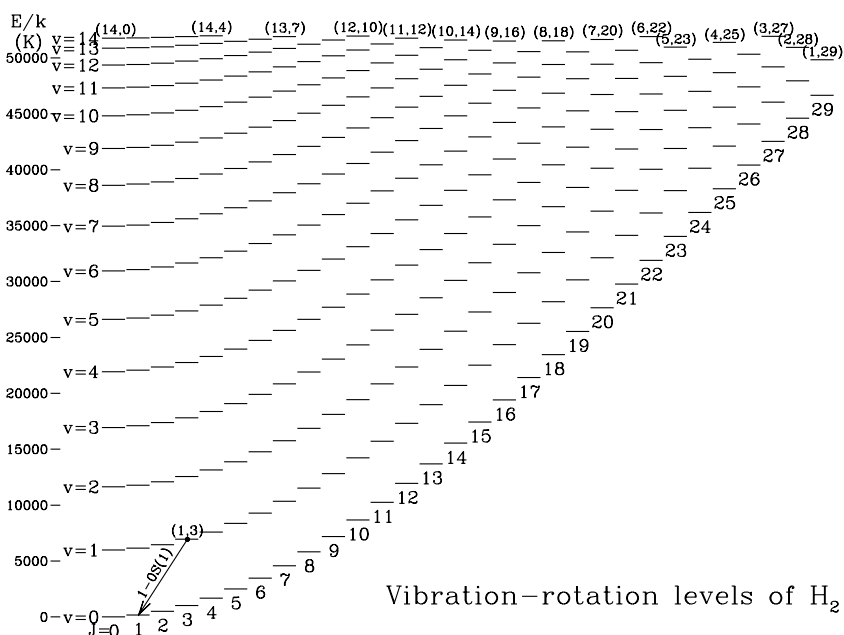
Figure 5.2 Vibration–rotation energy levels of the ground electronic state of H_2 with $J \leq 29$. The $(v, J) = (1, 3)$ level and 1–0S(1) $\lambda = 2.1218\,\mu\text{m}$ transition are indicated.

Because H_2 has no permanent electric dipole moment, the vibrational states and the rotational states radiate very weakly, via the time-variation of the electric quadrupole moment as the molecule vibrates or rotates. Because the nuclear spin state does not change, the rovibrational radiative transitions of H_2 must have $\Delta J = 0$ or $\Delta J = \pm 2$ – i.e., ortho→ortho or para→para.

The vibration–rotation emission spectrum of H_2 therefore consists of electric quadrupole transitions. The downward transitions are identified by

$$
\begin{aligned}
v_u - v_\ell \ \ \mathrm{S}(J_\ell) & \quad \text{if } J_\ell = J_u - 2 \ \ , \\
v_u - v_\ell \ \ \mathrm{Q}(J_\ell) & \quad \text{if } J_\ell = J_u \ \ , \\
v_u - v_\ell \ \ \mathrm{O}(J_\ell) & \quad \text{if } J_\ell = J_u + 2 \ \ .
\end{aligned}
$$

For example, 1–0 S(1) refers to the transition $(v=1, J=3) \to (v=0, J=1)$. This transition is indicated in Fig. 5.2.

5.1.7 CO

CO has 2 p electrons contributed by C and 4 p electrons contributed by O; together, these 6 p electrons fill the $2p$ subshell, and as a result, the ground electronic state of CO has zero electronic angular momentum and zero electronic spin: $^1\Sigma_0^+$, just like H_2. The reduced mass of CO is $(12 \times 16/28)\,\mathrm{amu} \approx 6.9\,\mathrm{amu}$. The C=O chemical bond is extremely strong; r_0 is unusually small, the spring constant k is unusually large, and the electric dipole moment (only $\mu = 0.110\,\mathrm{D}$) is unusually small. The fundamental vibrational frequency corresponds to a wavelength $\lambda_0 = c/\nu_0 \approx 4.6\,\mu\mathrm{m}$. (The energy is $\sim 50\%$ of the energy in the H_2 fundamental frequency.) The fundamental rotational frequency $2B_0/h = 115\,\mathrm{GHz}$, and $\hbar^2/Ik \approx 5.5\,\mathrm{K}$ (versus $170\,\mathrm{K}$ for H_2). Because the moment of inertia of CO is much larger than that of H_2, the rotational levels of CO are much more closely spaced than those of H_2, and therefore there are many more allowed rotation–vibration levels.

If μ is the permanent electric dipole moment, the Einstein A coefficient for a rotational transition $J \to J-1$, radiating a photon with energy $\hbar\omega$, is given by

$$
A_{J \to J-1} = \frac{2}{3} \frac{\omega^3}{\hbar c^3} \mu^2 \frac{2J}{2J+1} \tag{5.4}
$$

$$
= \frac{128\pi^3}{3\hbar} \left(\frac{B_0}{hc} \right)^3 \mu^2 \frac{J^4}{J + \frac{1}{2}} \ \mathrm{s}^{-1} \tag{5.5}
$$

$$
= 1.07 \times 10^{-7} \frac{J^4}{J + \frac{1}{2}} \ \mathrm{s}^{-1} \tag{5.6}
$$

$$
= 7.16 \times 10^{-8} \ \mathrm{s}^{-1} \quad \text{for } J = 1 \to 0 \ . \tag{5.7}
$$

5.1.8 ⋆ OH and Λ-Doubling

OH is an example of a molecule with the ground electronic state having nonzero electronic orbital angular momentum: with seven electrons, the OH ground state has $L_{ez} = 1$ and $S_{ez} = 1/2$, and is therefore designated by $^2\Pi_{1/2,3/2}$. The electron spin and orbital angular momenta can couple to give $J_e = 1/2$ or $3/2$, with energies that are separated due to spin-orbit coupling (i.e., fine-structure splitting in atoms or ions); the $J_e = 3/2$ state has the lower energy.

Now consider either one of these fine-structure states. The projection of the electron angular momentum along the nuclear axis is a constant of the motion, but the vector angular momentum $\mathbf{J}_e$ of the electrons is not. The electric field from the nuclei exerts a torque on the electrons. If the nuclei were held fixed in space, the electron angular momentum vector would precess in a cone centered on the nuclear axis. Now, of course, the nuclei are not held fixed, and if the electron angular momentum $\mathbf{J}_e$ changes, there must be an equal and opposite change in the angular momentum of the nuclei.

For the moment, ignore the nuclear spin – if the nuclear angular momentum is going to change, the nuclei must be undergoing rotation. The implication is that the nuclei undergo rotation even when the OH is in the ground state. Since there is no external torque applied to the OH, the electron angular momentum $\mathbf{J}_e$ and the nuclear angular momentum $\mathbf{J}_n$ both precess around the fixed total angular momentum $\mathbf{J} = \mathbf{J}_n + \mathbf{J}_e$. The magnitude of the total angular momentum J is just equal to the magnitude of the electronic angular momentum that is found when the nuclei are imagined to be held fixed.[1]

If additional angular momentum is given to the nuclei, the rotational kinetic energy will be increased, and each of the fine structure states of OH will have a "rotational ladder": the $J_e = 1/2$ state can have total angular momentum $J = 1/2$, 3/2, 5/2, 7/2, ..., and the $J_e = 3/2$ state can have $J = 3/2$, 5/2, 7/2, ..., and so on. The two rotational ladders are shown in Figure 5.3.

For the moment, let us reexamine the electronic wave functions in the idealization where the nuclei are held fixed, so that the electrons are moving in a potential that is time-independent and symmetric around the nuclear axis. For a linear molecule such as OH, the electronic eigenfunctions are of the form $\psi(r, \theta, \phi) = e^{\pm i\Lambda\phi} f(r, \theta)$, where Λ is the projection of the electronic angular momentum along the nuclear axis, and (r, θ, ϕ) are spherical coordinates with the center of mass as origin and with the polar axis along the internuclear axis: for $\Lambda > 0$, there are two degenerate states. Taking orthogonal linear combinations of these eigenfunctions,

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[1]Imagine the nuclei being held fixed, with the electrons orbiting around the nuclear axis. If the nuclei are suddenly released, the total angular momentum will remain unchanged (and equal to the angular momentum of the electrons just prior to the moment of release) but will now be shared by the electrons and the nuclei.
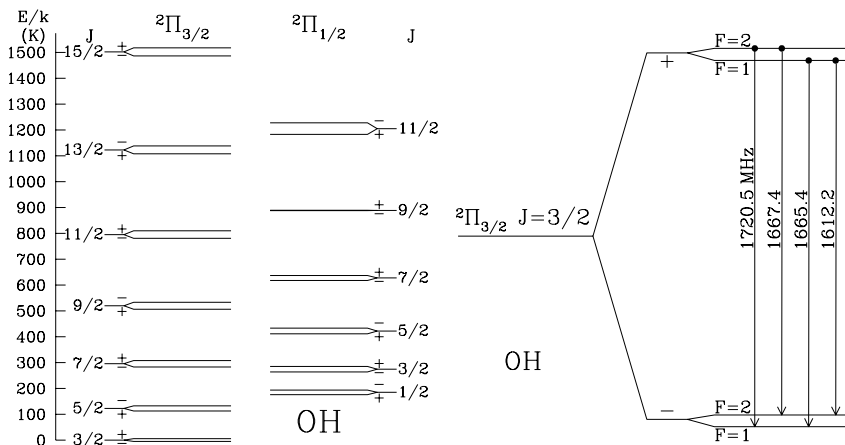
Figure 5.3 Energy levels of OH. Left: The rotational ladders of the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ electronic states. The splitting of the levels due to Λ-doubling has been exaggerated. Hyperfine splitting is not shown. Right: Λ-doubling and hyperfine splitting of the $^2\Pi_{3/2}(J=3/2)$ state, showing the four 18-cm lines. In a magnetic field, each of these four lines is further split by the Zeeman effect.

we have

$$\psi_+(r,\theta,\phi) = \frac{e^{i\Lambda\phi} + e^{-i\Lambda\phi}}{\sqrt{2}}\, f(r,\theta) = \sqrt{2}\cos(\Lambda\phi)f(r,\theta)\,, \qquad (5.8)$$

$$\psi_-(r,\theta,\phi) = \frac{e^{i\Lambda\phi} - e^{-i\Lambda\phi}}{i\sqrt{2}}\, f(r,\theta) = \sqrt{2}\sin(\Lambda\phi)f(r,\theta)\,. \qquad (5.9)$$

Now let the nuclear axis be in the $\hat{\mathbf{z}}$ direction, and let $\phi = 0$ correspond to the $\hat{\mathbf{x}}$ direction. The ψ_+ and ψ_- wave functions have different values of $\langle y^2 \rangle$. The moment of inertia of the molecule is dominated by the nuclei, but the electrons make a small contribution. If the rotational angular momentum is oriented along the x axis, the moment of inertia of the molecule, and therefore the rotational kinetic energy, will differ between the ψ_+ and ψ_- states: each of the energy levels is split by this "Λ-doubling" into two states with energies differing by of order $\Delta E_\Lambda \approx [m_e/(m_{AB})] \times [J^2\hbar^2/m_{AB}r_0^2]$, where m_e is the electron rest mass, m_{AB} is the reduced mass of the two nuclei, and r_0 is the internuclear separation. For the OH ground state $^2\Pi_{3/2}(J=3/2)$, the Λ-doubling splitting amounts to $\Delta E_\Lambda = 6.9 \times 10^{-6}$ eV, corresponding to a frequency $\Delta E_\Lambda/h = 1666$ MHz.

5.1.9 ⋆ Hyperfine Structure

Many nuclei have nonzero nuclear spin (e.g., ^{1}H, ^{13}C, ^{15}N, and ^{17}O), and, therefore, also have nuclear magnetic moments of magnitude $\sim \mu_N$, where $\mu_N \equiv$

$e^2\hbar/2m_pc$ is the nuclear magneton. The magnetic field from the nuclear magnetic moment couples to the electron motions, and, therefore, the electronic energy depends on the orientation of the nuclear moment and the electron angular momentum. This introduces hyperfine structure in the molecular energy levels. The eigenstates will be states of fixed *total* angular momentum $\mathbf{F} = \mathbf{J} + \mathbf{S}_n$, where $\mathbf{J}$ is the combined angular momentum of the electrons and rotational angular momentum of the nuclei, and S_n is the nuclear spin.

In the case of OH, with $S_n = 1/2$, we have seen that the two rotational ladders have $J = 3/2$, 5/2, 7/2, ..., and $J = 1/2$, 3/2, 5/2, and so on. Each of these states is first split by Λ-doubling into levels denoted $+$ or $-$; each of these levels is in turn split by hyperfine splitting into two levels, with $F = J \pm 1/2$. Therefore, the ground fine-structure level of OH $^2\Pi_{3/2}$ (with $J_e = 3/2$) splits into four sublevels, shown in Figure 5.3.

Radio frequency transitions between the sublevels can be observed in emission and absorption. These levels are important not only because they often are observable as masers (therefore, very bright tracers of the dynamics of molecular gas) but also because the energy levels are subject to Zeeman splitting; because these are radio frequency transitions, the Zeeman splitting produces a frequency shift that is measurable. OH is often used to measure the magnetic field strength in molecular clouds.

5.2⋆ Energy Levels of Nonlinear Molecules

When we consider nonlinear molecules, the rotational spectrum becomes considerably more complex. Treating the nuclei as point masses at fixed separations (the "rigid rotor" approximation), the moment of inertia tensor has three nonzero eigenvalues and three **principal axes.**

The rotational kinetic energy of a classical rigid rotor can be written

$$E_{\text{rot}}^{(\text{class.})} = \frac{(J_A\hbar)^2}{2I_A} + \frac{(J_B\hbar)^2}{2I_B} + \frac{(J_C\hbar)^2}{2I_C} \quad , \tag{5.10}$$

where I_A, I_B, and I_C are the three eigenvalues of the moment of inertia tensor, and $J_A\hbar$, $J_B\hbar$, and $J_C\hbar$ are the (instantaneous) projections of the total angular momentum $\mathbf{J}\hbar$ onto the three principal axes $\hat{A}$, $\hat{B}$, $\hat{C}$ corresponding to the eigenvalues I_A, I_B, I_C. It is conventional to define "rotation constants"

$$A \equiv \frac{\hbar^2}{2I_A} \quad , \quad B \equiv \frac{\hbar^2}{2I_B} \quad , \quad C \equiv \frac{\hbar^2}{2I_C} \quad , \tag{5.11}$$

so that the classical rotational kinetic energy is

$$E_{\text{rot}}^{(\text{class.})} = AJ_A^2 + BJ_B^2 + CJ_C^2 \quad . \tag{5.12}$$

Symmetric rotors, also referred to as "symmetric tops," have two degenerate eigenvalues; NH_3 is the primary example of astrophysical interest. Asymmetric rotors

(or asymmetric tops) have three nondegenerate eigenvalues – this applies to most polyatomic molecules of astrophysical interest, e.g., H_2O and H_2CO.

5.2.1 ★ Symmetric Rotor: NH_3

For the classical symmetric rotor, we let $\hat{A}$ be the symmetry axis; then $I_B = I_C$, and we can write

$$
\begin{aligned}
E_{\text{rot}}^{(\text{class.})} &= \frac{(J_A\hbar)^2}{2I_A} + \frac{(J\hbar)^2 - (J_A\hbar)^2}{2I_B} \\
&= \frac{(J\hbar)^2}{2I_B} + (J_A\hbar)^2 \left(\frac{1}{2I_A} - \frac{1}{2I_B} \right) \\
&= BJ^2 + (A - B)K^2 \quad ,
\end{aligned}
\tag{5.13}
$$

where $K \equiv J_A$ is the projection of **J** onto the symmetry axis. A "prolate" rotor has $I_A < I_B$ $(A > B)$; an "oblate" rotor has $I_A > I_B$ $(A < B)$. NH_3 is a prolate rotor.

If we now shift from the classical to the quantum treatment, we need only to replace J^2 by the eigenvalue $J(J + 1)$:

$$
E_{\text{rot}} = BJ(J + 1) + (A - B)K^2 \quad .
\tag{5.14}
$$

The quantum symmetric rotor, therefore, has rotational energy levels specified by two quantum numbers, J and K. If J is an integer, then K can take on values $K = 0, 1, ...J-1, J$. The rotational level structure of NH_3 is shown in Figure 5.4.

The electric dipole moment of a symmetric rotor is parallel to axis $\hat{A}$. When $J > K$, $\hat{A}$ precesses around the fixed angular momentum **J**, with a time-varying electric dipole moment. As a result, NH_3 rotational levels with $J > K$ have allowed electric dipole transitions $(J, K) \rightarrow (J-1, K)$, with Einstein A coefficients typically of order 10^{-2} to $10^{-1}\,\text{s}^{-1}$.

However, when $J = K$, the molecule is spinning around its symmetry axis. Classically, this rotation state has no time-varying electric dipole moment, and would not produce electric dipole radiation. Quantum-mechanically, the levels $J = K$ are metastable, with very long radiative lifetimes. The sequence of levels $J = K$ are referred to as the "rotational backbone"; at interstellar densities, most of the NH_3 will be found occupying these levels, with only very small populations in the levels with $J > K$ above the backbone.

Because NH_3 is a hydride, it has a very small moment of inertia, and the rotational transitions are at relatively high (microwave) frequencies.

However, NH_3 has an additional type of transition that is purely quantum mechanical in nature. Consider the plane defined by the three H atoms. There are two minimum energy positions for the N atom, symmetrically located on either side of the plane. When the problem is treated quantum mechanically, it is found that there are two distinct eigenstates for the NH_3 wave function, separated slightly in
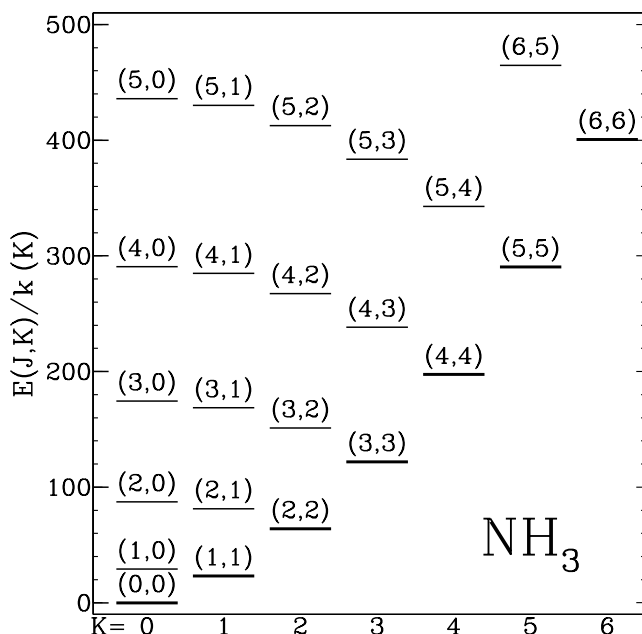
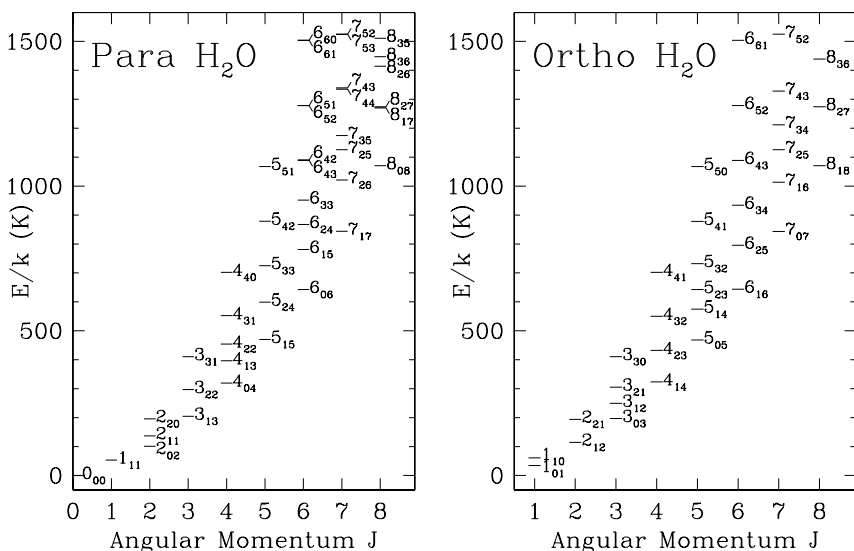**Figure 5.4** Rotational energy levels of NH_3 with $K \leq 6$ and $E/k < 500$ K. Each level, labeled by (J, K), is split into two inversion sublevels (not shown). Levels with $J = K$ [e.g., (0,0), (1,1), (2,2), (3,3), ...] are referred to as the "rotational backbone".

energy [9.8×10^{-5} eV in the case of the (1,1) level]. Transitions between these two eigenstates are referred to as **inversion lines**, because the frequency of the transition corresponds to the characteristic frequency for the N atom to tunnel back and forth through the H atom plane from one energy minimum to the other, with associated time-varying electric dipole moment. Transitions between these inversion sublevels are observable, with frequencies near 23 GHz; for the backbone levels $(J, K) = (1, 1)$ and $(2, 2)$, the inversion lines are at 23.694 and 23.723 GHz, respectively.

The inversion sublevels of the (J, K) states are, in turn, further split by interactions with the electric quadrupole moment of the ^{14}N nucleus and the magnetic dipole of the protons. The electric quadrupole splitting breaks the $(1, 1)$ inversion transition into six separate lines, spread over 3.06 MHz – the splitting is large compared to the thermal line broadening, and therefore these lines are easily resolved. Each of these lines is, in turn, split by hyperfine splitting, but the hyperfine splitting is only on the order of 10 to 40 kHz, corresponding to Doppler shifts of only 0.13 to 0.5 km s^{-1}.

NH_3 is not the only molecule with observable inversion transitions. Inversion transitions of H_3O^+ near 181 μm have also been observed (Goicoechea & Cernicharo 2001; Yu et al. 2009).

Figure 5.5 Rotational energy levels of para-H_2O (left) and ortho-H_2O (right) with total angular momentum $J \leq 8$ and $E/k < 1500\,K$.

5.2.2⋆ Asymmetric Rotor: H_2O

We turn now to the more complicated case of the general asymmetric rotor, with three nondegenerate eigenvalues. We order them $I_A < I_B < I_C$, so that the rotation constants $A > B > C$. The total angular momentum J is of course a constant of the motion, but the projections of J onto individual axes are no longer conserved, except for the special case where $J_A = J$ or $J_C = J$. For the general case where $J_A < J$ and $J_C < J$, the asymmetric rotor undergoes a tumbling motion, with the instantaneous values of J_A, J_B, and J_C all varying while satisfying $J_A^2 + J_B^2 + J_C^2 = J^2$.

For a given value of J, the allowed rotation states are specified by two indices, K_{-1} and K_{+1}; the rotational state is designated $J_{K_{-1},K_{+1}}$. There are seven $J = 3$ states: 3_{03}, 3_{12}, 3_{13}, 3_{21}, 3_{22}, 3_{30}, and 3_{31}.

In the case of H_2O, the two protons can have their nuclear spins either antiparallel or parallel, corresponding to total nuclear spin either 0 or 1. Just as for H_2, the antiparallel spin state is referred to as "para," and the parallel spin state as "ortho." Because the overall wave function must be antisymmetric under proton exchange, it turns out that para-H_2O must have $K_{-1} + K_{+1}$ odd, while ortho-H_2O must have $K_{-1} + K_{+1}$ even. Because the nuclear spins do not change in radiative transitions, ortho-H_2O and para-H_2O behave almost like separate species. The rotational levels of para-H_2O and ortho-H_2O are shown in Figure 5.5.

The selection rules for electric dipole radiative transitions are $\Delta J = 0, \pm 1$; $\Delta K_{-1} = \pm 1, \pm 3$; and $\Delta K_{+1} = \pm 1, \pm 3$.

The allowed radiative decays tend to build up the populations in the lowest energy level for a given J – these states are referred to as the **rotational backbone**. All of the rotational backbone levels (except the lowest) have allowed transitions to the next lower backbone state. For most of the backbone states, this is the only allowed downward transition. However, two of the ortho-H_2O backbone states in Fig. 5.5 – 4_{14} and 6_{16} – have permitted downward transitions to nonbackbone levels: $4_{14} \rightarrow 3_{21}$ and $6_{16} \rightarrow 5_{23}$. The nonbackbone levels tend to have very low populations, and, therefore, these two transitions, with the upper level on the backbone and the lower level above the backbone, frequently have population inversions with resulting maser emission in the $4_{14} \rightarrow 3_{21}$ transition at 380 GHz and the $6_{16} \rightarrow 5_{23}$ transition at 22.2 GHz.

The same holds true for the 3_{13} and 5_{15} levels of para-H_2O: the $3_{13} \rightarrow 2_{20}$ 183 GHz and $5_{15} \rightarrow 4_{22}$ 325 GHz transitions are also candidates for masing.

5.3⋆ Zeeman Splitting

If an external magnetic field $\mathbf{B}$ is present, molecular energy levels with a magnetic moment $\boldsymbol{\mu}$ will be shifted in energy by an amount

$$\Delta E_{\mathrm{mag}} = -\boldsymbol{\mu} \cdot \mathbf{B} , \qquad (5.15)$$

where $\boldsymbol{\mu}$ is the magnetic moment, with contributions from the orbital and spin angular momenta of the electrons. When both spin and orbital angular momentum are present, neither $\mathbf{S}$ nor $\mathbf{L}$ are fixed in space – both precess around the total angular momentum $\mathbf{F}\hbar = (\mathbf{L} + \mathbf{S})\hbar$. The magnetic moment is antiparallel to $\mathbf{F}$,

$$\boldsymbol{\mu} = -g\mu_{\mathrm{B}}\mathbf{F} , \qquad (5.16)$$

where $\mu_{\mathrm{B}} \equiv e\hbar/2m_e c$ is the **Bohr magneton**, and g is the **Landé g-factor**. Values for the Landé g-factor lie between 0.5 and 1, depending on the values of L and S.

The projection of $\mathbf{F}$ onto the direction of the magnetic field $\mathbf{B}$ is M_F, with $2F+1$ allowed values $M_F = -F, -F + 1, ..., F$. The perturbation to the energy level is

$$E_{\mathrm{mag}} = (g\mu_{\mathrm{B}}B) M_F . \qquad (5.17)$$

For a transition between two levels with different M_F, the energy-level splitting $g\mu_{\mathrm{B}}B$ corresponds to a frequency shift

$$(\Delta\nu)_B = \frac{\Delta E_{\mathrm{mag}}}{h} = \frac{g\mu_{\mathrm{B}}}{h} \Delta M_F B \qquad (5.18)$$

$$= 1.3996 \, g \, \Delta M_F \frac{B}{\mu G} \, \mathrm{Hz} . \qquad (5.19)$$

For interstellar magnetic fields in the $\mu G - mG$ range, Eq. (5.19) shows that the frequency shifts are small, typically much smaller than the frequency shift $(\Delta v/c) \times \nu$

due to Doppler broadening.[2] The only hope for detecting this small shift is to (1) use radio frequency transitions where $(\Delta\nu)_B/\nu$ is large enough for the shifts to be measured, and (2) to use the fact that the two circularly polarized components have $\Delta M_F = \pm 1$, so that they are shifted in frequency by $2(\Delta\nu)_B$. If Doppler broadening is assumed to contribute identically to the two circular polarizations, then subtraction of one circular polarization from the other produces a signal that allows the frequency shift $(\Delta\nu)_B$ to be measured, allowing the magnetic field strength to be determined.

Successful detection of the Zeeman splitting requires an atom or molecule with a strong radio frequency transition, and $F > 0$. The hydrogen atom fulfills this requirement, with $F = 1/2$ in the ground state $^2S_{1/2}$, Landé g-factor $g = 0.5$, and the spin-flip transition at $\nu = 1.420\,\text{GHz}$.

Diatomic molecules with $^2\Pi_{1/2,3/2}$ orbitals have both $F > 0$ (so that Zeeman splitting occurs) and Λ-doubling (providing relatively low frequency radio transitions). The OH transitions at 1.665 and 1.667 GHz are frequently used, both in absorption and in (maser) emission. Higher frequency OH transitions can also be used, as well as CH transitions at 3.33 GHz.

In high-density regions, OH and CH may be unavailable, and it becomes necessary to resort to rotational transitions with much higher frequencies. The CN 1–0 rotational transition at 113 GHz has been used for Zeeman measurements.

Polyatomic molecules also exhibit Zeeman splitting. H_2O does not have an unpaired electron, and hence $F = 0$, but ortho-H_2O, with parallel proton spins, has a small magnetic moment contributed by the protons. Magnetic field measurements have been made using H_2O masers in the $6_{16} \rightarrow 5_{23}$ transition at 22.2 GHz. Further information can be found in reviews by Heiles et al. (1993) and Heiles & Crutcher (2005).

5.4 Further Reading

Bransden & Joachain (2003) has an extensive discussion of molecular quantum mechanics and spectroscopy.

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[2]The only exception appears to be OH – the 1.67 GHz frequency (due to Λ-doubling) is low, and regions hosting OH masers appear to sometimes have large enough magnetic fields to produce frequency shifts exceeding the line width.

Chapter Six

Spontaneous Emission, Stimulated Emission, and Absorption

In this chapter, we review the general principles governing absorption and emission of radiation by absorbers with quantized energy levels. The absorbers in question can be atoms, ions, molecules, dust grains, or *any* objects with energy levels.

6.1 Emission and Absorption of Photons

If an absorber X is in a level ℓ and there is radiation present with photons having an energy equal to $E_u - E_\ell$, where E_ℓ and E_u are the energies of levels ℓ (for "lower") and u (for "upper"), the absorber can absorb a photon and undergo an upward transition:

$$\textbf{absorption}: \qquad X_\ell + h\nu \to X_u , \quad h\nu = E_u - E_\ell . \qquad (6.1)$$

Suppose that we have number density n_ℓ of absorbers X in level ℓ. The rate per volume at which the absorbers absorb photons will obviously be proportional to both the density of photons of the appropriate energy and the number density n_ℓ, so we can write the rate of change of n_ℓ due to photoabsorption by level ℓ as

$$\underbrace{\left(\frac{dn_u}{dt}\right)_{\ell \to u}}_{\text{populate level } u} = \underbrace{-\left(\frac{dn_\ell}{dt}\right)_{\ell \to u}}_{\text{depopulate level } \ell} = n_\ell B_{\ell u} u_\nu , \quad \nu = \frac{E_u - E_\ell}{h} , \quad (6.2)$$

where u_ν is the radiation energy density per unit frequency, and the proportionality constant $B_{\ell u}$ is the **Einstein B coefficient**[1] for the transition $\ell \to u$.

An absorber X in an excited level u can decay to a lower level ℓ with emission of a photon. There are two ways this can happen:

$$\textbf{spontaneous emission}: \qquad X_u \to X_\ell + h\nu \quad \nu = (E_u - E_\ell)/h , \quad (6.3)$$

$$\textbf{stimulated emission}: \quad X_u + h\nu \to X_\ell + 2h\nu \quad \nu = (E_u - E_\ell)/h . \quad (6.4)$$

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[1] Einstein was the first to discuss the statistical mechanics of the interaction of absorbers with the quantized radiation field.