

Molecular Structure & Spectroscopy

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1. Introduction

We have so far considered the formation of photoionized regions in the interstellar medium, which have been studied for the longest time. However, star formation occurs inside dense molecular clouds. Therefore it is essential for us to understand these environments, and the physics that occurs as ultraviolet radiation from young stars encounters molecular gas. These subjects require us to first investigate the physics and spectroscopy of molecules. This is the subject of today's lecture.

We will start by investigating the degrees of freedom of diatomic molecules. We will subsequently describe their electronic, vibrational, and rotational spectra. We conclude with a brief description of polyatomic molecules.

The following references may be helpful:

BRIEF: Appendix #6 of Osterbrock & Ferland
 Ch. 2 of Dopita & Sutherland

LONGER DESCRIPTIONS:

I. Levine, *Molecular Spectroscopy*: The book your professor learned from as a student. This is really a full one-term course on the subject.

The NIST molecular spectroscopy website (see link from class page) has some tutorials and lots of data.

2. Diatomic Molecules

A diatomic molecule has two nuclei and some number of electrons. It will be discussed at length here as it is the simplest type of molecule; in addition, the most abundant molecules in the ISM (H_2 and CO) are diatomic. Its basic degrees of freedom are:

- *Translational*: The motion of the center of mass (3dof).
- *Electron orbital*: The electrons have a spatial wave function.
- *Electron spin*: The unpaired electrons carry spin.
- *Vibrational*: The bond can stretch or compress (1dof).
- *Rotational*: With the center of mass fixed, the direction of the bond can change (2dof).
- *Nuclear spin*: In the case of homonuclear molecules, and occasionally with radio transitions, the nuclear spin degree of freedom is often important.

The translational degrees of freedom are trivially separated. The others represent internal degrees of freedom of the molecule and are important to the physics that we will use in the next lecture. We will discuss electronic structure first since it is most closely related to the physics of atoms.

A. ELECTRONIC STRUCTURE

Electrons in molecules occupy **molecular orbitals**. Just as for atoms, the orbitals can be classified by their symmetry properties. In particular, if we work in cylindrical coordinates with the nuclei lying along the z-axis, then the orbitals will have a dependence $\sim e^{im\phi}$, where m is the projection of the angular momentum onto the **internuclear axis**. An orbital is designated as a σ -orbital if $m=0$, a π -orbital if $m=\pm 1$, and a δ -orbital if $m=\pm 2$. The σ orbitals are usually nondegenerate, but the π , δ , etc. orbitals come in pairs of equal energy ($\pm m$).

A diatomic molecule may have two identical nuclei, in which case it is called **homonuclear** (otherwise it is **heteronuclear**). Homonuclear molecules also possess parity symmetry, under which a particular orbital may be even or odd. This is designated with a "g" subscript for even orbitals and a "u" for odd, e.g. σ_g , σ_u , etc.

With the exception of H_2^+ , molecules have multiple electrons and hence have a total value of the angular momentum projected onto the internuclear axis. This is denoted by the quantum number Λ . If $\Lambda=0$, then reflection through a plane containing the nuclei will multiply the overall wave function by either +1 or -1; that level of the molecule is then denoted as either "+" or "-." Note that a single electron in a σ orbital always has + symmetry, so H_2^+ can have no $\Lambda=0, -$ levels. Also note that $|\Lambda|\neq 0$ levels are doubly degenerate (reflection can always give a state with $-\Lambda$).

Finally, in a multielectron molecule, the electrons may have unpaired spins, and hence have a quantum number S denoting the total spin of the electrons. For closed-shell molecules, $S=0$, but radicals (e.g. CH), odd-electron species (e.g. NO), and paramagnetic even-electron species (e.g. O_2) have nonzero electron spin.

All of these symmetry properties are designated by the **molecular term symbol**, which is of the form $^{2S+1}\Lambda_{u,g}^{\pm}$. The electron spin is treated in the same way as for atoms; the orbital angular momentum (projected onto the internuclear axis) is denoted with a Greek letter (Σ , Π , Δ , etc.); and the \pm superscript applies only to Σ levels. Examples of term symbols are as follows.

Ground state of H_2^+ :

The single electron is in the lowest-energy orbital, which has no nodes and is a σ orbital. It is symmetric under parity (which exists since H_2^+ is homonuclear), so this is a g orbital, and with a single electron there is a $+$ symmetry. The lone electron has spin $S=1/2$. Thus the term symbol is $^2\Sigma_g^+$.

Ground state of H_2 :

Now there are two electrons, both in the lowest σ_g orbital. Their orbital wave function is symmetric, so the spin wave function must be antisymmetric, giving spin $S=0$. Thus the term symbol is $^1\Sigma_g^+$.

Ground state of HeH^+ :

This molecule has two electrons, and like H_2 they both occupy the lowest orbital. However, there is no parity symmetry in this molecule, so the term symbol is $^1\Sigma^+$.

More generally, all molecules in which each energy level is completely filled have fully paired electrons ($S=0$), an equal number in positive and negative angular momentum orbitals ($\Lambda=0$), and have term symbols $^1\Sigma_g^+$ (homonuclear) or $^1\Sigma^+$ (heteronuclear). This is analogous to noble gas structures (although the close spacing of molecular orbitals may make such species much more reactive than noble gases!). Examples include CO, CS, N_2 , etc.

Ground state of O_2 :

The O_2 molecule has orbitals formed from the symmetric and antisymmetric linear combinations of the atomic orbitals on each O atom. The ordering of orbitals is:

2p	σ_u	—	
2p	π_g	—	—
2p	π_u	—	—
2p	σ_g	—	
2s	σ_g	—	
2s	σ_u	—	

1s σ_u —
 1s σ_g —

The 16 electrons fill the lowest orbitals, with two unpaired electrons in the π_g orbital. Thus the parity symmetry will be g. Hund's rules tell us that the electrons will go into the higher-spin ($S=1$) state, so the orbital wave function must be antisymmetric. Since both the $m=+1$ and -1 orbitals have one electron, $\Lambda=0$. Finally, the antisymmetric combination of the π_g orbitals has $-$ symmetry. Thus the term symbol is ${}^3\Sigma_g^-$.

Excited states of O₂:

The lowest excited states of O₂ will have the electrons in $S=0$, so they occupy a symmetric combination of the π_g orbitals. This may be either a case of both having the same sign angular momentum, ${}^1\Delta_g$, or opposite sign, ${}^1\Sigma_g^+$.

A molecule may have multiple states corresponding to the same term; these are distinguished with letters in front of the term symbol. The ground state always receives the letter *X*: e.g. the ground state of O₂ would be written $X{}^3\Sigma_g^-$. The letters denoting excited states are historical and follow no discernable pattern.

B. ROTATION

We now consider the motion of the nuclei in the **Born-Oppenheimer approximation**, i.e. treating the electronic wave function as evolving adiabatically as the nuclei move. The rotation of a closed-shell molecule involves the motion of the nuclei as well as the electrons. It can be treated to a first approximation like a rigid rotator (we will investigate vibration later). This gives rise to angular momentum quantum numbers J and M and an angular wave function $\sim Y_{JM}(\theta, \varphi)$, with energy levels $\hbar^2 J(J+1)/2I$, where I is the moment of inertia. The parity is $(-1)^J$, in accordance with the parity of the spherical harmonic. Typical moments of inertia are $\sim \text{few} \times 10^4 m_e a_0^2$, leading to energy levels in the microwave ($\sim 10^{11}$ Hz) for small J .

A molecule with nonzero Λ or S exhibits more complicated behavior. In this case, one must distinguish several types of angular momentum:

Angular momentum	Total	Projection on internuclear axis
Electron orbital	L	Λ
Electron spin	S	Σ
Total orbital	N	Λ (No nuclear orbital a.m. axis)
Total orbital + spin	J	Ω

We have already described the quantum numbers Λ and S . We also know that J is conserved. In order to identify the energy levels, however, we must consider two limiting cases:

Hund Case (a): The precession of the electron spin around the internuclear axis (due to relativistic effects) is faster than the molecular rotation. (Example: OH.)

Hund Case (b): The precession of the electron spin around the internuclear axis is slower than the molecular rotation (Example: H₂⁺.)

In the Case (a) molecules, Σ is a conserved quantum number, and hence so is $\Omega = \Lambda + \Sigma$. For example, OH is a ²Π molecule and so the possible values of Ω are 1/2 and 3/2 (and their negatives – see later). We therefore know that J must be at least as large as $|\Omega|$ and have the same character (either integer or half-integer). For a given value of J , the squared angular momentum perpendicular to the internuclear axis is $J(J+1) - \Omega^2$.

We know that for each value of $|\Omega|$ the above analysis gives two sets of energy levels for each J . Since the parity transformation reverses the sign of Ω , there is (for $\Omega \neq 0$) one positive parity and one negative parity level. The degeneracy between them is broken by a multitude of corrections associated with finite nuclear:electron mass ratio, etc.

In the Case (b) molecules, N is a conserved quantum number. A similar argument to the above shows that N is an integer, and is at least $|\Lambda|$. For $\Lambda \neq 0$, there are two degenerate levels, one of positive and one of negative parity, a phenomenon known as **Λ-doubling**. The total angular momentum J takes on values from $|N-S|$ to $N+S$ in steps of $\Delta J=1$.

C. VIBRATION

We next consider vibration. The molecule has a natural frequency of vibration, $\omega = (k/\mu)^{1/2}$, where k is the force constant of the bond and μ the reduced mass. The vibrational energy is $E_{\text{vib}} = (v+1/2)\hbar\omega$, where the vibrational quantum number $v=0,1,2,\dots$. Typical vibrational frequencies are in the mid-IR: $\sim 10^{14}$ Hz, or somewhat less for bonds between two metal atoms. In diatomic molecules, vibration has no effect on the symmetry properties, etc.

The above discussion presumes a harmonic potential for vibrations. In reality, the molecule has a dissociation energy, and as it is approached the vibration becomes anharmonic, with energy levels spaced closer than $\hbar\omega$. A similar result occurs for rotation. In particular, the finite dissociation energy means that a molecule has a finite number of rotation-vibration levels in any electronic state.

D. NUCLEAR SPIN

Nuclear spin has a tiny effect on molecular energy levels and may lead to hyperfine splitting (e.g. in the ground state of ¹⁶O¹H). But it can have a much more profound effect on homonuclear molecules because nuclei obey wave function antisymmetrization or symmetrization depending on their spin.

As an extreme example, consider a closed-shell homonuclear molecule such as H₂. In this case, swapping the spatial positions of the nuclei introduces a $(-1)^J$

into the wave function. Correspondingly the proton spins for H₂ must be symmetric ($I=1$) for odd J and antisymmetric ($I=0$) for even J . Thus there are two different types of H₂: **para-H₂** (even J) and **ortho-H₂** (odd J). They can only interconvert by swapping protons or flipping a nuclear spin. Moreover, they have different statistical weights: ortho-H₂ has three nuclear spin states while para-H₂ has only one.

An even more extreme realization of the same facts occurs for molecules such as ⁴He₂⁺ (ground term: ²Σ_g⁺; Case *b*), where the nuclei have spin 0. In this case, wave function symmetrization implies the spatial wave function must be symmetric. Thus the odd- N levels of the ground electronic state of ⁴He₂⁺ *simply do not exist!*

3. Radiation from Diatomic Molecules

We are now ready to consider the selection rules for radiation from diatomic molecules. We may consider three types of transitions: rotational, vibrational, and electronic, in order of increasing energy. In the latter cases, the quantum numbers associated with lower-energy phenomena also may change, e.g. a vibrational transition is often accompanied by a change in angular momentum.

In all cases, the exact selection rules apply. For example, in electric dipole transitions (the most common type), we must have $|\Delta J| \leq 1$ and a change in parity.

A. ROTATION SPECTRA

We focus on the rotation spectra of closed-shell molecules in their ground electronic and vibrational state. The typical transitions are electric dipole decays with $\Delta J = -1$. The frequency of the emitted photon can be obtained by subtracting the energies of the levels:

$$\nu = \frac{1}{h} \left[\frac{\hbar^2 J_u (J_u + 1)}{2I} - \frac{\hbar^2 (J_u - 1) J_u}{2I} \right] = \frac{h}{4\pi I} J_u.$$

The quantity $h/8\pi I$ is often denoted by B and is called the **rotational constant**. The spectral lines of the molecule are at frequencies $2B$, $4B$, $6B$, etc.: they are evenly spaced. A slight deviation from this pattern occurs due to rotational deformation of the molecule (the bond lengthens as the molecule rotates faster), so that at high quantum numbers the frequencies are packaged more closely together.

The decay rate is obtained from the usual formula,

$$A_{J \rightarrow J-1} = \frac{4\omega^3}{3c^3} \sum_{M_f} \left| \langle J-1, M_f | \boldsymbol{\mu} | JM_i \rangle \right|^2.$$

Here $\boldsymbol{\mu}$ is the dipole moment operator. The matrix element is an integral over the spherical harmonics, which evaluates to

$$A_{J \rightarrow J-1} = \frac{4\omega^3}{3c^3} \sum_{M_f} \left| \langle J-1, M_f | \boldsymbol{\mu} | JM_i \rangle \right|^2 = \frac{4\omega^3 \mu^2}{3c^3} \sum_{M_f} \left| \int \mathbf{n} Y_{J-1, M_f}^*(\mathbf{n}) Y_{JM_i}(\mathbf{n}) d^2\mathbf{n} \right|^2 = \frac{4\omega^3 \mu^2}{3c^3} \frac{J}{2J+1}.$$

We can see that the decay rates rise rapidly with J (due to the ω^3).

A special case occurs for homonuclear molecules such as H_2 , since these have zero dipole moment. In this case, decay occurs through electric quadrupole transitions with $\Delta J = -2$. The frequencies are then $6B$, $10B$, $14B$, etc. and the decay lifetimes are much longer. In practical ISM cases, H_2 is the only homonuclear molecule with sufficient abundance for the quadrupole transitions to be of interest.

The rotational spectral lines are often labeled with a letter denoting the type of transition (R for electric dipole decays, S for quadrupoles) and the angular momentum of the lower level in parentheses. For example:

$$\begin{array}{llll} \text{H}_2 \text{ S}(0) & J = 2 \rightarrow 0, & \text{CO R}(3) & J = 4 \rightarrow 3, \\ \text{H}_2 \text{ S}(1) & J = 3 \rightarrow 1. & & \end{array}$$

Some cases of particular interest are:

H_2 : The quadrupole lines are at:

S(0)	28 μm	[Radiation from lowest excitation of para- H_2]
S(1)	16 μm	[Radiation from lowest excitation of ortho- H_2]

Rotational constants:¹

Molecule	$2B$
$^{12}\text{C}^{16}\text{O}$	115.3 GHz
$^{13}\text{C}^{16}\text{O}$	110.2 GHz
$^{12}\text{C}^{32}\text{S}$	49.0 GHz

The carbon monoxide dipole series is usually the strongest of the molecular lines.

B. VIBRATION SPECTRA

A vibrating molecule can often be approximated as a harmonic oscillator. In a true harmonic oscillator whose dipole moment is a linear function of position, there is a selection rule that the quantum number v changes by 1, however in practice molecular potentials are anharmonic and larger $|\Delta v|$ is common. A perfectly harmonic oscillator would emit at frequencies v equal to the natural frequency of oscillation, however in an anharmonic oscillator the frequency changes with excitation (generally becoming lower for potentials with a finite dissociation energy). Thus $v=1 \rightarrow 0$ and $2 \rightarrow 1$ do not quite coincide.

Molecular rotation splits the vibrational lines of a molecule into a band. To see this, we note that the value of J for upper and lower levels is not the same. We

¹ From the NIST database:

<http://physics.nist.gov/PhysRefData/MolSpec/Diatomic/index.html>

focus first on closed-shell molecules. Selection rules tell us that for electric dipole transitions, $J_u - J_l = \pm 1$ (0 is parity forbidden for the closed shell case). In a decay, the frequency is given by the sum of both the change in vibrational energy and the change of rotational energy:

$$\nu = \nu_{\text{vib}} + B[J_u(J_u + 1) - J_l(J_l + 1)] = \begin{cases} \nu_{\text{vib}} + 2B(J_l + 1) & J_u - J_l = +1 \\ \nu_{\text{vib}} + 2B - J_l & J_u - J_l = -1 \end{cases}$$

The solution with $J_u = J_l + 1$ emits at higher frequency and is called the **R-branch**, while the solution with $J_u = J_l - 1$ is at lower frequency and is called the **P-branch**. Each is made up of many lines corresponding to different values of J_l . The individual rotation-vibrational lines are denoted by e.g.

CO 0—1 R(3),

in which the two numbers indicate the vibrational quantum numbers (lower level given first by convention), then the type of branch (P or R) and then the angular momentum of the lower level.

In special cases, $J_u - J_l$ may be different from ± 1 . The two examples are:

- Electronic states with open shells, in which two levels with the same J may have different parity. In this case, $J_u - J_l = 0$ is possible. This is called a **Q-branch**.
- Electric quadrupole transitions, as occurs with the vibrations of homonuclear molecules, most importantly H_2 . For this case, the selection rules allow $J_u - J_l = 0, \pm 2$. The latter cases give rise to O- and S-branches.

Among the most important molecular vibration lines are those of H_2 . In particular, the H_2 1—2 S(1) line at 2.247 μm falls in a wavelength range observable from the ground. It is therefore of great interest to observations of molecular gas (although a source of excitation is needed to see the vibrational lines).

C. ELECTRONIC SPECTRA

Physics very similar to that for vibrational spectra occurs for electronic spectra. The upper and lower states of the molecule are of different electronic states, and there are no exact vibrational selection rules. The electronic states do however obey the usual selection rules from atomic physics: $|\Delta\Lambda| \leq 1$; no $\Sigma^+ \rightleftharpoons \Sigma^-$; and for homonuclear molecules, the parity (g or u) must change.

Every molecule has a very large number of electronic transition lines, since there are many possible combinations of rotation and vibration quantum numbers involved. Interpretation of molecular electronic spectra (e.g. UV absorption by H_2) therefore requires detailed modeling to determine which lines will be most important.

D. HYPERFINE STRUCTURE

Finally, nuclear spins introduce the possibility of hyperfine splittings in non-closed-shell molecules. The classic case is OH, whose ground term symbol is $^2\Pi$. Precession of the electron spin around the internuclear axis splits the $\Sigma=1/2$ and $3/2$ levels (Hund case *a*) and the $\Sigma=3/2$ case has lower energy. The state is doubled so that both + and - parity are present for the lowest angular momentum ($J=3/2$); it turns out that the - parity has lower energy. Finally, the proton spin couples with the orbital + electron spin angular momentum to give $F=1$ (lower) or 2 (upper).

The + and - parity states of OH are connected by an electric dipole transition that in circumstellar environments can be strong enough for maser action.² Hyperfine structure splits this line into 4 components at 1612, 1665, 1667, and 1720 MHz.

4. Polyatomic Molecules

We will only briefly discuss the physics of polyatomic molecules due to their complexity. We may consider two cases: linear and nonlinear molecules.

A. LINEAR MOLECULES

A linear molecule (e.g. HCN, CO₂) is in many ways similar to a diatomic molecule: the key difference is that it has many more vibrational degrees of freedom, and from a symmetry perspective it is important that some of these can bend the molecule (i.e. the vibrational excitations can carry angular momentum!). However, the *rotation* spectrum, which is all that we will discuss here, is similar to that of a diatomic; we need only consider the appropriate moment of inertia.

We note that some linear molecules have zero dipole moment by symmetry and hence no rotation spectrum (e.g. CO₂). Such molecules do develop dipole moments when deformed so they do show vibrational spectra.

The rotational constants for some linear molecules found in the ISM are:³

Molecule	$2B$
$^1\text{H}^{12}\text{C}^{14}\text{N}$	88.6 GHz
$^1\text{H}^{12}\text{C}^{16}\text{O}^+$	89.2 GHz

Of particular interest is that due to their small number of rotational states, one can search efficiently for the microwave rotational transitions of quite large linear molecules. This is how the interstellar cyanopolyynes (HC₃N, HC₅N, HC₇N, HC₉N, HC₁₁N) were discovered.

² See discussion in Dopita & Sutherland, §4.4.

³ From the NIST database:

<http://physics.nist.gov/PhysRefData/MolSpec/Diatomic/index.html>

B. NONLINEAR MOLECULES

The vast majority of molecules are nonlinear (H_2O , NH_3 , CH_4 , CH_3OH , etc.). In some cases, they have symmetries that allow classification of their electronic states (e.g. H_2O has two mirror planes). They have $3N-6$ vibrational modes, where N is the number of atoms, and hence there is a whole forest of rotation-vibrational lines. Such lines from H_2O (and other species) make infrared observations impossible from the ground in much of the infrared spectrum.

The transitions of greatest significance in the ISM are associated with rotation. These are easily excited at the low temperatures in molecular clouds and appear in the microwave part of the spectrum. The rotation of a polyatomic molecule is determined by its principle axes of inertia: $I_A < I_B < I_C$.

The rotational levels may be very complex to describe. However, there are some special cases:

Spherical moments of inertia:

A molecule such as CH_4 has $I_A = I_B = I_C$. In this case, we may choose any axis fixed to the molecule and find that the projection of angular momentum on this axis K ($K = -J \dots +J$) and onto the laboratory z-axis M ($M = -J \dots +J$) are conserved. Thus each value of J has a degeneracy $(2J+1)^2$. However, the degeneracies of some levels may be modified by nuclear spin statistics (e.g. CH_4 $J=0$ is nonexistent). More importantly, the same symmetries that give rise to a spherical moment of inertia tensor generally give rise to zero dipole moment, so e.g. CH_4 does not have a rotation spectrum.

Oblate molecules:

If the moment of inertia tensor has an axis of symmetry (e.g. $I_A = I_B$), its total angular momentum J and the projection onto the C-axis K ($K = -J \dots +J$) are conserved. Each J and K corresponds to a $2J+1$ -fold degenerate level due to different values of M .

If $I_A = I_B < I_C$ (e.g. NH_3)⁴ the energy levels are:

$$E = \frac{\hbar^2}{2I_A} J(J+1) - \left[\frac{\hbar^2}{2I_A} - \frac{\hbar^2}{2I_C} \right] K^2.$$

The levels with $K \neq 0$ have twice the normal degeneracy, $2(J+1)$. The symmetry that sets $I_A = I_B$ implies the dipole moment is along the C-axis. This implies the selection rule that $\Delta K = 0$ (in addition to the usual $|\Delta J| \leq 1$). Thus for the oblate molecules, the frequencies of the rotational lines are at integer multiples of $h/4\pi I_A$, just as for linear molecules.

Nuclear spin statistics are also important in these molecules as they affect the degeneracies corresponding to different values of K .

⁴ The spectrum of NH_3 contains additional splittings because the molecule is flexible.

Prolate molecules:

If $I_A < I_B = I_C$ (e.g. CH_3CN), then the same argument applied to the oblate molecules is valid. However, in this case I_A and I_C are switched, so the sign of the second term in the energy equation is opposite.

Triaxial molecules:

Finally, some molecules have 3 different moments of inertia (e.g. H_2O). There is no analytic formula for their energy levels.

The usual description of the energy levels of a triaxial molecule is to imagine adiabatically distorting the molecule so that $I_B \rightarrow I_A$ (oblate). The resulting projection of angular momentum onto the C-axis (conserved for an oblate molecule) is K_C . Similarly, one may distort the molecule to a prolate configuration and obtain a projection K_A . There are $2J+1$ levels (the number cannot change under adiabatic deformations) and this is the number of possible values of (K_A, K_C) . Their pattern is best shown by example: for $J=4$, the ordering is:

$J_{K_A K_C}$:	4 ₄₀	highest
	4 ₄₁	
	4 ₃₁	
	4 ₃₂	
	4 ₂₂	
	4 ₂₃	
	4 ₁₃	
	4 ₁₄	
	4 ₀₄	lowest.

The selection rules depend on the direction of the dipole moment relative to the principal axes. There are also nuclear spin statistics issues: e.g. in H_2O , there are two proton spins. It is found in this case that ortho- H_2O may only exist for $K_A + K_C$ odd, and para- H_2O for $K_A + K_C$ even.