

# Lecture 9. Fundamentals of Molecular Spectroscopy and Scattering Theory <sup>①</sup>

2/14/2006

## I. Introduction

\* By now, we have introduced the Quantum Mechanics, Atomic Structure, Atomic Spectra, Laser Spectroscopy with Atoms.

These provide a good understanding to the resonance fluorescence phenomenon and its potential applications in laser remote sensing.

\* Besides resonance fluorescence (usually with atomic spectroscopy), there are other molecular spectroscopy applied in laser remote sensing, and they are closely related to scattering processes.

\* This lecture is aimed to introduce the knowledge about molecular spectroscopy and scattering theory.

\* List of Contents for this lecture and next lecture:

1. Molecular Structure (qualitatively)
2. QM Explanation of Molecular Structure
3. Molecular Transition Probability
4. QM General Theory of Scattering
5. Light Scattering with molecules
6. Infrared / Raman Spectroscopy
7. Classification of Light Scattering.

## II. Molecular Structure

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### 1. Qualitative description.

A molecule consists of two or more atoms. The interactions among atoms form strong chemical bonds, and keep these atoms together as one body — a molecule.

The chemical bond is mainly formed by the interactions among outer electrons. Core electrons with the shell of each atom usually do not contribute to the molecular chemical bond. After forming a molecule, the outer electron states undergo huge change, and cause very different energy levels and spectra.

Above descriptions can be seen from spectroscopy:

(1) As we mentioned before, if core (inner) electrons of an atom have transition, ~~the~~ X-ray photons will be produced. Similar thing is true with molecular inner electrons. On spectroscopy, there is almost no difference between atomic X-ray and molecular X-ray, which means that inner electrons do not have much state change even if atoms are ~~are~~ bounded to each other to form a molecule.

(2) But ~~the~~ normal molecular spectra (caused by outer electrons) are ~~so~~ completely different from atomic spectra,

which means the dramatic change of outer electron states when atoms form a molecule.

Inside a molecule, there are several different motions. These motions, in principle, are not independent, but affect each other. However, the frequency of each motion is so different from one another. It is precise enough in most cases to consider these motions separately.

The three main motions are

- ① outer electrons → forming chemical bond
- ② vibration around a balance point
- ③ whole molecule rotates around axes.

Motion	Transition Frequency	Energy (ev)	Spectra
Electronic State	UV or Visible	1-20	electronic Spectra
Molecular Vibration	near infrared	0.05-1	rotation-vibration Spectra
Molecular Rotation	far infrared and microwave	$10^{-4}$ -0.05	rotation Spectra

In a first approximation, the energy of a molecule can be represented as the sum of three parts—the electronic, the vibrational, and the rotational energy:

$$E = E_e + E_v + E_r \quad (1)$$

In Fig. 10 the vibrational and rotational levels in two electronic states are represented schematically.

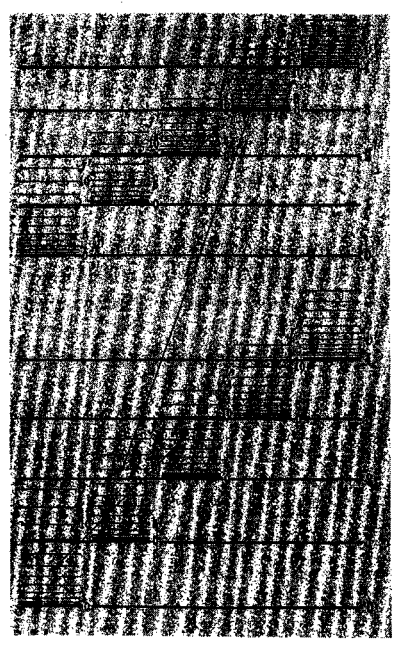


Fig. 10. Vibrational and rotational levels of two electronic states A and B of a molecule (schematic).

The three double arrows indicate examples of transitions in the pure rotation spectrum, the rotation-vibration spectrum, and the electronic spectrum of the molecule.

(4)

## 2. QM Description

A complete description of any molecular state would involve a number of different degrees of freedom, each with its own coordinates. First, there is translation of the molecule as a whole; then the complex motion of the outer electrons with respect to the nuclei; then vibration and rotation of the nuclei with respect to each other; Finally, electron and nuclear spin. The energy eigenvalue equation (i.e., time-independent Schrödinger equation) can be used to express this:

$$\left[ -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_K \frac{\hbar^2}{2M_K} \nabla_K^2 + V(\vec{r}_i, \vec{R}_K) \right] |\psi\rangle = E |\psi\rangle \quad (1)$$

Where:  $-\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2$  is electron kinetic energy operator  
( $m_e$  - electron mass;  $i$  - summing over several electrons)

$\sum_K \frac{\hbar^2}{2M_K} \nabla_K^2$  is nuclear kinetic energy operator  
( $M_K$  - nuclear mass;  $K$  - summing over several nuclei)

$V(\vec{r}_i, \vec{R}_K)$  - total potential energy operator, which depends on the coordinates of all of the electrons ( $\vec{r}_i$ ) and nuclei ( $\vec{R}_K$ )

Common method to analyze these motions is to divide these motions to two parts (1) the relatively slow motion of the nuclei, and (2) the much faster motion of the electrons around nuclei. The physical basis of this decomposition stems from the fact that electron mass is much smaller than that of any nucleus ( $M_K/m_e \geq 1800$ ).

This is called "Born-Oppenheimer Approximation".

Total wave function  $\Psi$  can be expressed as a product of an electronic wave function  $\Psi_e(\dots, \vec{r}_i, \dots, \vec{R}_k, \dots)$  and a nuclear wave function  $\Psi_N(\dots, \vec{R}_k, \dots)$ :

$$\Psi = \Psi_e(\vec{r}_i, \vec{R}_k) \Psi_N(\vec{R}_k) \tag{2}$$

$\Psi_N$  is essentially independent of electron coordinates  $\vec{r}_i$ , but  $\Psi_e$  is dependent on  $\vec{r}_i$  and  $\vec{R}_k$ . But considering the main terms, and neglect minor terms, Eq. (1) can be decomposed to:

$$\sum_i \nabla_i^2 \Psi_e + \frac{2me}{\hbar^2} (E_e - V_e) \Psi_e = 0 \tag{3}$$

$$\text{and } \sum_k \frac{1}{M_k} \nabla_k^2 \Psi_N + \frac{2}{\hbar^2} (E - E_e - V_N) \Psi_N = 0. \tag{4}$$

where,  $E_e$  is the energy eigen value of the electron system,

$$\boxed{V = V_e + V_N} \leftarrow \text{assumption.} \tag{5}$$

\* The solution of Eq. (3) are quite complex even for the simplest molecules. In general, the solutions lead to molecular orbitals that result in a series of electronic states

$\Sigma, \Pi, \Delta, \Phi, \dots$  (just as with atoms S, P, D, F, ...),

which are characterized by the quantization of the electron's angular momentum and the symmetry properties of the states. (Detailed analysis can be found in a series

of books by Herzberg:

«Molecular Spectra & Molecular Structure»

Volume I. Spectra of Diatomic Molecules

Volume II. Infrared and Raman Spectra of Polyatomic Molecules

Volume III. Electronic Spectra and Electronic Structure of Polyatomic Molecules

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If all the degrees of freedom are independent from one another, the total energy of the molecule can be expressed as a simple sum of the individual contributions from each of the freedom degree,

$$E_{\text{total}} = E_{\text{trans}} + E_{\text{electronic}} + E_{\text{vib}} + E_{\text{rot}} + E_{\text{spin}}. \quad (6)$$

This requires each term in the Hamiltonian operator corresponding to each mode commute so that

$$\Psi_{\text{total}} = \Psi_{\text{trans}} \Psi_{\text{electronic}} \Psi_{\text{vib}} \Psi_{\text{rot}} \Psi_{\text{spin}} \quad (7).$$

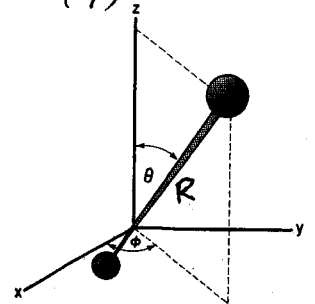
This is not exactly true in reality, but very close. For most cases, we do not care  $E_{\text{trans}}$  (translation energy) and  $E_{\text{spin}}$ , but are more concerned about the rest three terms, i.e.,  $E = E_{\text{electronic}} + E_{\text{vib}} + E_{\text{rot}}. \quad (8)$

$E_{\text{electronic}}$  is determined by Eq. (3), and mainly determined by the electron motions about nuclei. The electronic states usually have large energy separation, e.g., for most molecules, the transition frequency between the ground electronic state and the first excited electronic state is over 4 eV, corresponding to short UV wavelength.

$E_{\text{vib}}$  and  $E_{\text{rot}}$  are determined by Eq. (4), and mainly determined by the motions of nuclei. For a diatomic molecule,

$$\Psi_N = \frac{1}{R} \Psi_{\text{vib}}(R) \Psi_{\text{rot}}(\theta, \phi) \quad (9)$$

where  $R$  is inter-nuclear separation,  $\theta, \phi$  are angular coordinates.



From Eq. (4), we have

$$-\frac{\psi_{\text{rot}}}{R^2} \frac{\partial}{\partial R} \left\{ R^2 \frac{\partial}{\partial R} \left( \frac{\psi_{\text{vib}}}{R} \right) \right\} - \frac{\psi_{\text{vib}}}{R^3} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi_{\text{rot}}}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi_{\text{rot}}}{\partial \phi^2} \right] + \frac{2\mu}{\hbar^2} [E_N - V(R)] \frac{\psi_{\text{vib}} \psi_{\text{rot}}}{R} = 0 \quad (10)$$

where  $\mu = \frac{M_1 M_2}{M_1 + M_2}$  the reduced mass of the nuclei,

$$E_N = E - E_{\text{electronic}}$$

Rotational component of the Hamiltonian operator

$$\hat{H}_{\text{rot}} = -\frac{\hbar^2}{2\mu R^2} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right], \quad (11)$$

so we have:  $\hat{H}_{\text{rot}} \psi_{\text{rot}} = E_J \psi_{\text{rot}}, \quad (12)$

where  $E_J$  is the rotational eigen energy;

$$E_J = \frac{\hbar^2}{2\mu R^2} J(J+1). \quad (13)$$

Here,  $J$  is the rotational quantum number,

$$J = 0, 1, 2, \dots, +\infty.$$

Therefore, Eq. (10) can be rewritten as

$$\frac{\psi_{\text{rot}}}{R} \left[ -\frac{\partial^2 \psi_{\text{vib}}}{\partial R^2} + \frac{2\mu}{\hbar^2} [E_N - E_J - V(R)] \psi_{\text{vib}} \right] = 0 \quad (14)$$

$$\Rightarrow -\frac{\partial^2 \psi_{\text{vib}}}{\partial R^2} + \frac{2\mu}{\hbar^2} [E_{\text{vib}} - V(R)] \psi_{\text{vib}} = 0$$

This is a one-dimensional oscillator  $\Rightarrow$  vibration motion

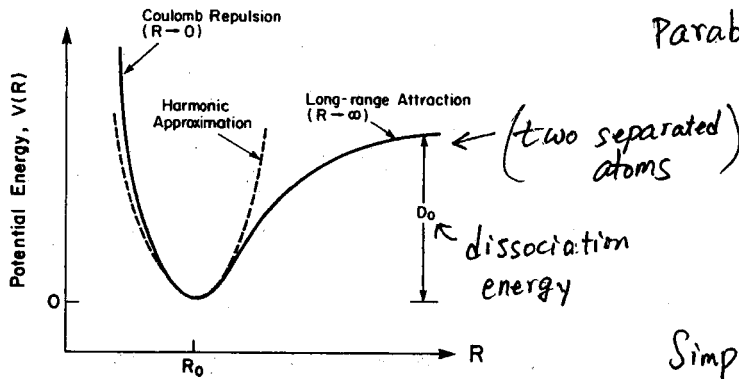
$$E_{\text{vib}} = E_N - E_J.$$

Therefore, a diatomic molecular Schrödinger equation can be

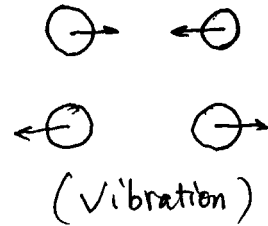
split into two one for the rotational mode, the other for vibration.

# \* Vibrational state of a diatomic molecule.

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Parabolic potential approximation.



Simple harmonic oscillator:

$$E_{vib} = \hbar\omega \left( v + \frac{1}{2} \right)$$

where  $v$  is the vibrational quantum number.  
 $v = 0, 1, 2, \dots$

$$\omega = \sqrt{\frac{k}{\mu}}$$

$k$  is effective restoring-force constant,  
 $\mu$  is the reduced mass of nuclei.

angular frequency of the harmonic oscillator.  
 $\left( \frac{1}{2} \hbar\omega \right)$  - zero-point energy.  
 Equally spaced energy for ideal harmonic.

Fig. 3.4. Harmonic approximation to a diatomic molecular potential curve  $V(R)$ .

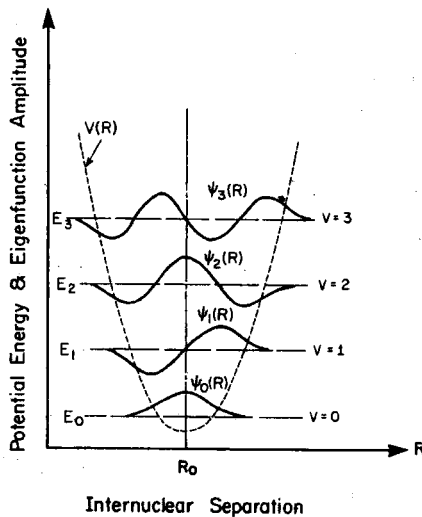


Fig. 3.5. Vibrational eigenfunctions  $\psi_v(R)$  and potential-energy curve  $V(R)$  (broken) for a diatomic molecule that is well represented by a simple harmonic oscillator.

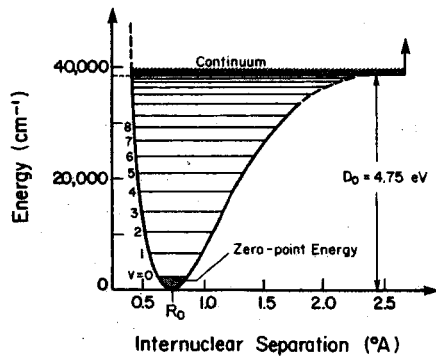


Fig. 3.6. Potential energy and vibrational levels for the electronic ground state of hydrogen (Herzberg, 1950).

The departure of the molecular potential from that of the ideal

harmonic oscillator (i.e., the anharmonicity) leads primarily to a decrease in the energy spacing between adjacent vibration states as  $v$  increases.  
 Allowed vibrational energy:  $E_v = \hbar\nu \left( v + \frac{1}{2} \right) - \hbar\nu x_e \left( v + \frac{1}{2} \right)^2 + \dots$



# \* Rotational States of a Diatomic Molecule

(9)

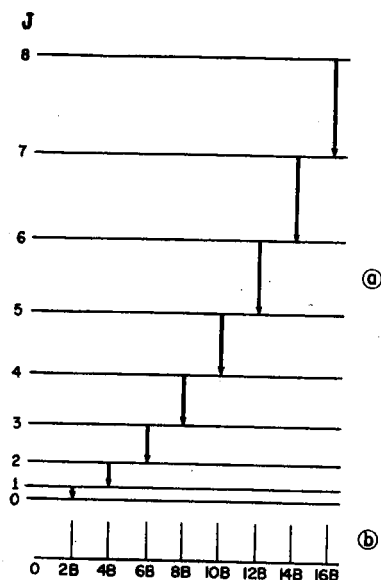


Fig. 3.7. (a) Rotational energy-level structure of a rigid diatomic molecule. (b) Schematic of the corresponding rotational spectrum.

If we assume the molecule is rigid, so the inter-nuclear separation is fixed at its equilibrium distance  $R_0$ ,

$$E_J = \frac{\hbar^2}{2\mu R_0^2} J(J+1)$$

where  $J$  is the rotational quantum number.

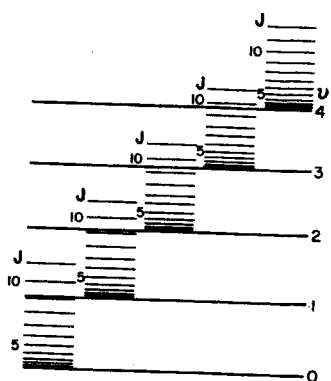


Fig. 3.8. Energy levels of a vibrating rotator. A number of rotational levels are shown for each of the first five vibrational levels (Herzberg, 1950).

Of course, the molecule is not rigid, and will vibrate around its equilibrium point. Then the rotation is affected by the vibration. This leads us to the vibrating rotator model.

This vibrating rotator could be understood as the rotations at each vibration eigen state (each vibration eigenstate has an equilibrium  $R_v$ ).

## III. Molecular Spectra.

(10)

Now we consider the radiative transitions with molecules. A molecule radiatively decays from an upper energy eigenstate to a lower energy eigenstate:

$$|b v'' J''\rangle \rightarrow |a v' J'\rangle$$

$a, b$  - electronic states

$v', v''$  - vibrational quantum numbers

$J', J''$  - rotational quantum numbers

} for lower & upper states.

Corresponding the three kinds of energy, we have three kinds of spectra:

(a) rotation spectra, in which transitions take place from the rotational levels of a given vibrational level in a given electronic state to other rotational levels of the same vibrational and electronic state.

(b) rotation-vibration spectra, in which transitions take place from the rotational levels of a given vibrational level to the rotational levels of another vibrational level of the same electronic state.

(c) electronic spectra, in which transitions <sup>take place</sup> from the rotational levels of the various vibrational levels of one electronic state to the rotational and vibrational levels of another electronic state.

In addition, radio-freq. and microwave spectra have been observed between certain fine-structure levels of a given rotational and vibrational level of a given electronic state. (due to electron spin or nuclear spin)

The transition probability in molecular spectra is also determined by the matrix element of the dipole moment.

$$\langle \hat{d}(bv''J'' \rightarrow av'J') \rangle \equiv \langle bv''J'' | \hat{d} | av'J' \rangle.$$

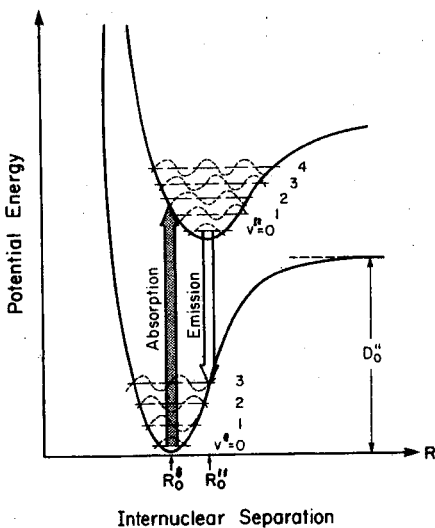
Dipole moment  $\hat{d} = \hat{d}_e + \hat{d}_N$

where  $\hat{d}_e = \sum_i (-e \hat{r}_i)$ , - electron dipole moment

$\hat{d}_N = \sum_K (eZ_K \hat{R}_K)$  - nuclear dipole moment.

We neglect the QM calculation, but only give results.

### (1) Electronic Spectra



Selection Rules:

$$\Delta \Lambda = 0, \pm 1$$

$$\Delta S = 0$$

Parity change

$\Lambda$ : total orbital angular momentum quantum number

$S$ : Spin quantum number

The transition lines are strong for  $\Delta v = v'' - v' = 0$  while  $\Delta v = \pm 1$  are weak.

This is called "Franck-Condon" principle: nuclear motion ( $\approx 10^{-13}$  s) can be regarded as "frozen" on the time scale of electronic transitions ( $\leq 10^{-15}$  s). As a consequence, transitions between electronic states of a molecule can be represented by vertical lines on the potential-energy diagram.

Each electronic state corresponds to one potential energy curve. So above diagram means two different electronic states.

(12)

For different electronic states, the equilibrium separations between two nuclei are different.

$R_0'$  is for the electronic ground state

$R_0''$  is for the electronically excited state.

$$R_0'' > R_0'$$

If a molecule initially resides in the  $v'=0$  vibrational state of the ground electronic state, the most probable transition is from  $v'=0$  to  $v''$  with high quantum number ( $v''=2$  in this diagram) that is just above  $R_0'$  with the same inter-nuclear separation. Therefore, the probability of  $|a, v'=0\rangle \Rightarrow |b, v''=2\rangle$  is strongest. — absorption.

The molecule then relaxes to  $v''=0$  state with inter-nuclear separation of  $R_0''$ . Now if transition occurs, the molecule will decay to  $v'=3$  state with the same inter-nuclear separation.

$$|b, v''=0\rangle \Rightarrow |a, v'=3\rangle \text{ is strongest.}$$

Note: each such transition corresponds to a spectral band, due to multiple rotational states.

Therefore, the most probable transition gives the intensity maximum in the spectral band.

The maximum of the emission spectra is redshifted relative to the maximum in the absorption spectra.

— This spectral shift is called Stokes Shift.

\* These electronic transitions are in short UV range, not very much interest to lidar from ground, but could be useful to lidar from space.

## (2) Vibration Spectra

(13)

These are transitions between different vibrational levels within the same electronic state.

The selection rules are

$$\Delta V = \pm 1$$

In a heteronuclear diatomic molecule, (e.g., OH) the molecule possesses a dipole moment, therefore, can emit or absorb photons when it undergoes a transition from one vibrational state to another. These transitions are usually in the infrared range, so it is called IR absorption/emission.

In a homonuclear molecule, (e.g., O<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>, ...), there is no dipole moment at any value of inter-nuclear separation, and consequently, such molecules neither absorb nor emit infrared radiation, although they can be vibrationally excited or deexcited through collisions.

The majority of our atmosphere O<sub>2</sub> and N<sub>2</sub> cannot absorb or emit infrared emission.

### 3) Rotation Spectra

Transitions between different rotational levels within the same vibrational and electronic state.

Selection rules:  $\Delta J = 0, \pm 1$ ,  
 $J' = 0 \leftrightarrow J'' = 0$

$$\vec{F} = \vec{J} + \vec{I}_1 + \vec{I}_2, \quad I_{1,2} \text{ nuclear spins}$$

$$\Rightarrow \Delta F = 0, \pm 1, \quad F' = 0 \leftrightarrow F'' = 0.$$

### 4) Rotation-Vibration Spectra

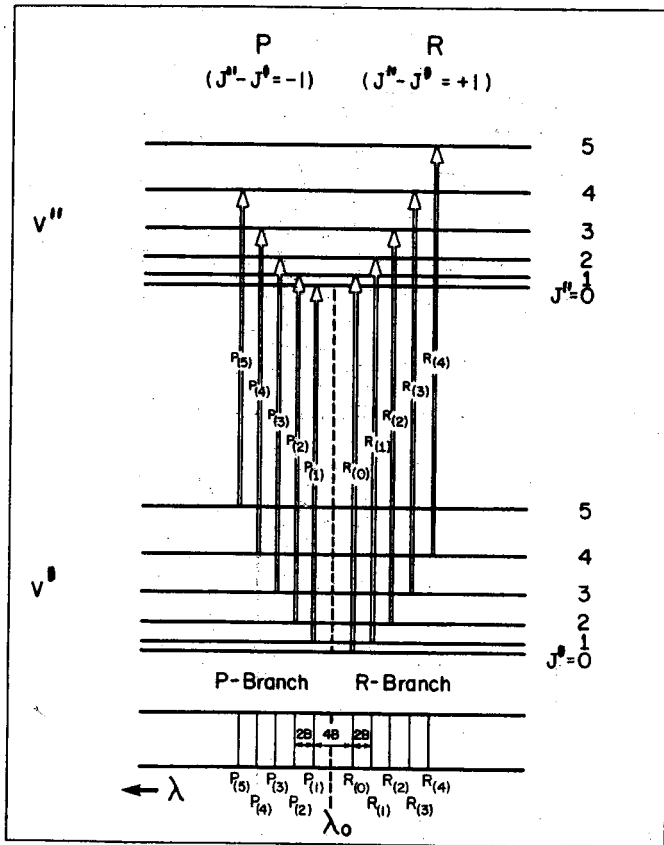


Fig. 3.9. Energy-level structure and rotational spectrum for a rigid rotator.

IR absorption/emission:  
 $\Delta V = \pm 1, \Delta J = \pm 1$

Raman Activity

$$\Delta V = 0, \pm 1$$

$$\Delta J = 0, \pm 2$$

P branch:  $\Delta J = J'' - J' = -1$

R  $\Delta J = +1$

O  $\Delta J = -2$

Q  $\Delta J = 0$

S  $\Delta J = +2$

~~Lecture 9. Fundamentals of Scattering Theory~~ 2/14/2006

~~\* QM General Theory of Scattering (Collision)~~

Elastic Scattering: only kinetic energy exchange,  
no change of internal state

Inelastic Scattering: accompanied by a change in  
the internal state of the colliding particles.

QM calculation of scattering probability and amplitude

\* Scattering Theory of light with air molecules

Another view on the scattering/collision problem —

a  $\hbar\omega$  photon is annihilated, and

a  $\hbar\omega_s$  photon is created.

if  $\omega_s = \omega \Rightarrow$  Elastic scattering

if  $\omega_s \neq \omega \Rightarrow$  Inelastic Scattering

\* Classification of Scattering (She's revisit + ...)