

# Spectroscopy

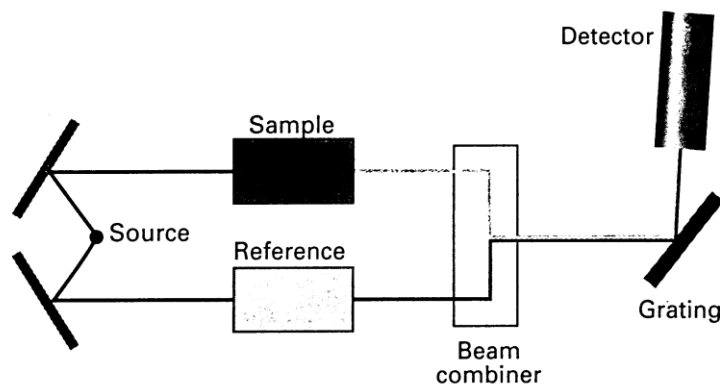
*using electromagnetic radiation to study atoms and molecules*

- ◆ one of the most important applications of quantum mechanics
- ◆ uses radiation to determine atomic and molecular properties
- ◆ provides molecular structures with extraordinary accuracy
- ◆ monitors molecular events on timescales down to femtoseconds
- ◆ many practical applications, including analytical chemistry

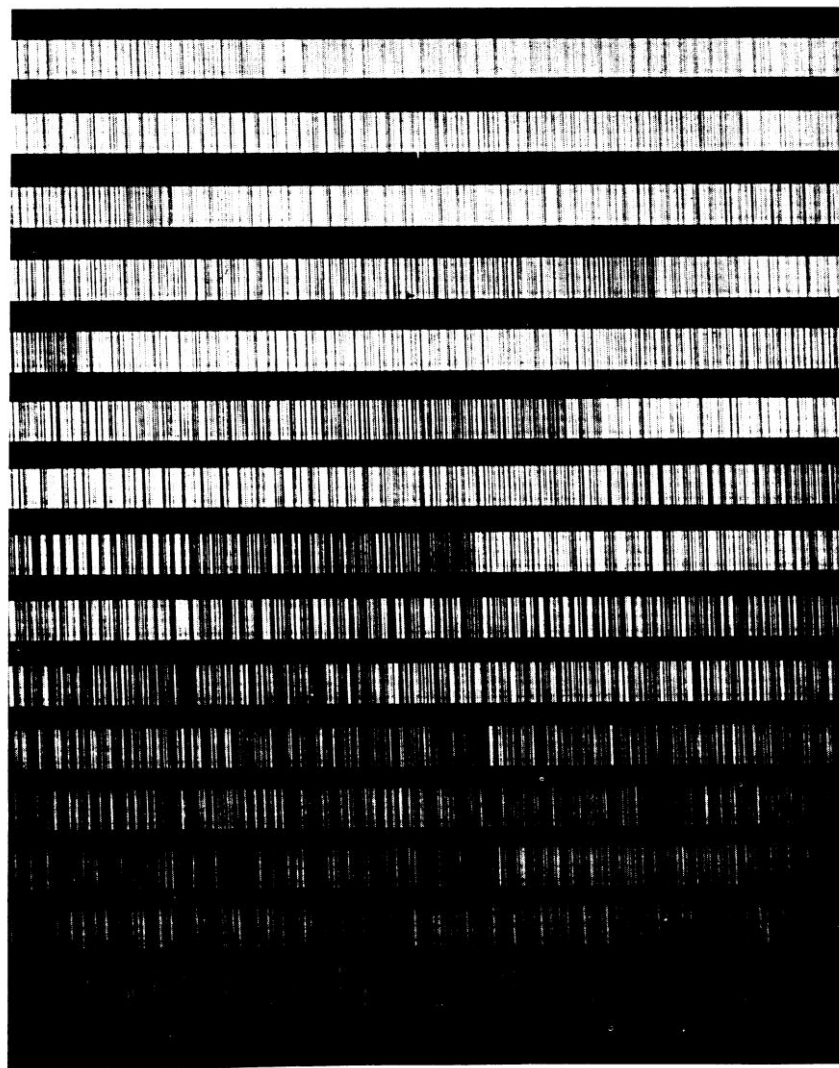
The fundamental idea behind spectroscopy: the energy of absorbed or emitted photons is related to the difference between the quantum mechanical energy levels of atoms or molecules involved in the transition

$$h\nu = hc/\lambda = hc\tilde{\nu} = |E_{\text{final}} - E_{\text{initial}}|$$

$\tilde{\nu} = 1/\lambda$  is the **wavenumber** of the radiation, the number of waves per unit length.



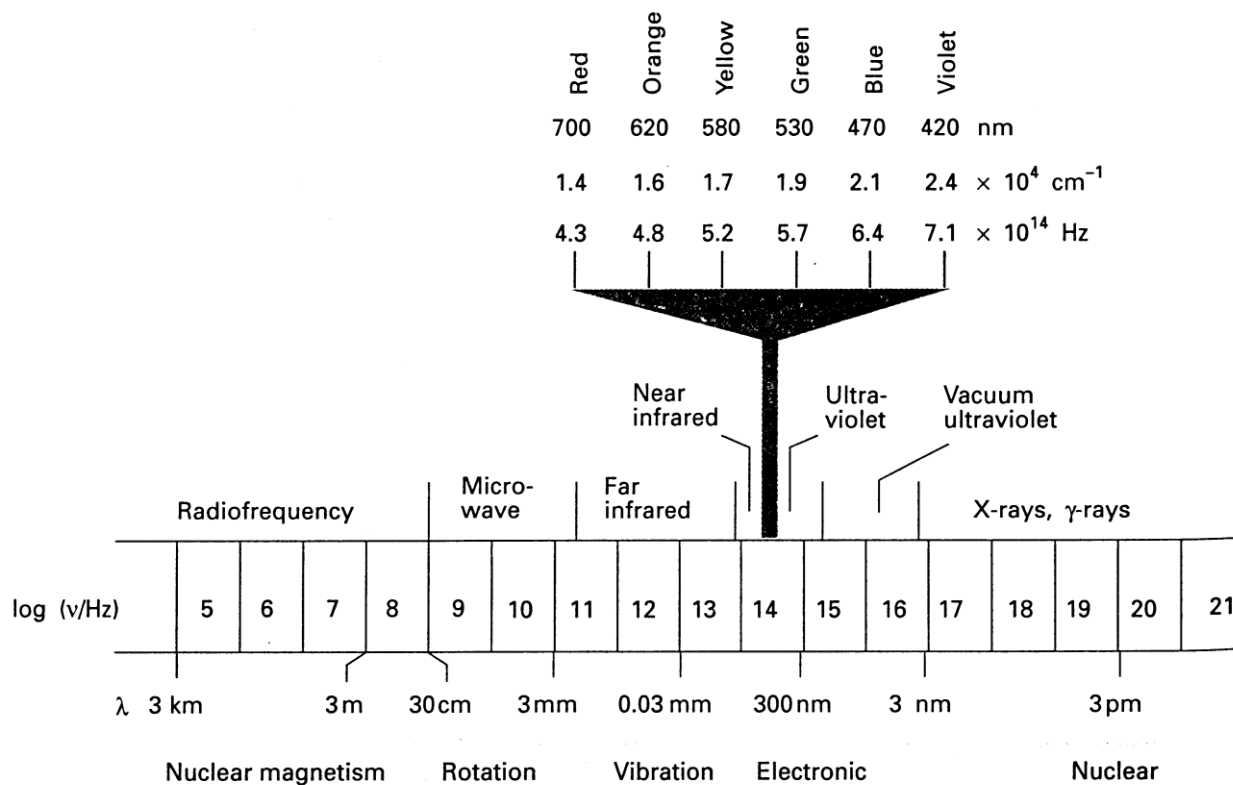
**A portion of the visible spectrum of iodine vapor:**



Every one of these transitions can be assigned to well defined initial and final quantum states!

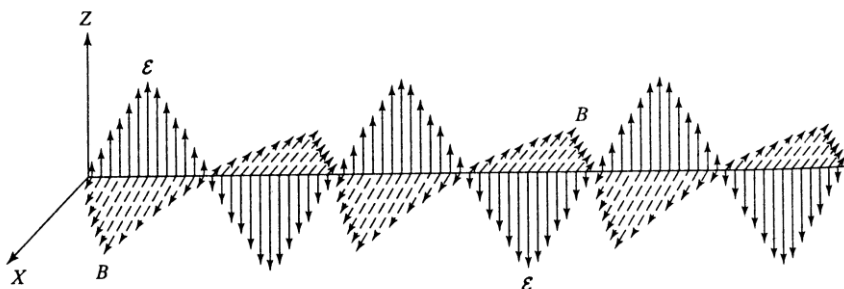
The energies of the photons indicate the kinds of transitions:

- radio-frequency**      transitions between nuclear spin states (nmr spectroscopy)
- microwaves**          transitions between rotational and electron spin states
- infrared**              vibrational transitions (superimposed on rotational states)
- visible/uv**            transitions between electronic energy levels
- x-rays**                ionization and bond dissociation
- gamma rays*            *nuclear energy levels*



The energy levels of atoms and molecules decide the **possible** frequencies and wavelengths of absorbed and emitted radiation for atomic and molecular transitions. But what transitions are **probable** (most intense)?

Electromagnetic radiation consists of propagating oscillations in the strengths of the electric and magnetic fields.



Atoms and molecules are collections of positively-charged nuclei and negatively-charged electrons. So, the strength of the interaction between electromagnetic radiation and atoms or molecules is governed the electric **dipole moment operator**

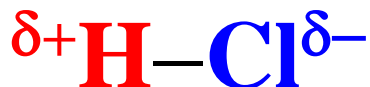
$$\hat{\mu} = \sum q_i \vec{r}_i$$

for the distribution of electrical charges  $q_i$  at positions  $\vec{r}_i$ . In SI units, an electric dipole is expressed in C m. In practice, the non-SI unit “Debye” is often used.

$$1 \text{ Debye} = 1 \text{ D} = 3.33564 \times 10^{-30} \text{ C m}$$

Molecules with large permanent dipoles (*i.e.*, large permanent separation of electrical charge, such as HCl) therefore interact relatively strongly with radiation

$$\leftarrow \hat{\mu} = 1.08 \text{ D}$$



producing the most intense (most probable) transitions. Molecules and atoms can also have fluctuating (transient) electric dipole moments that can interact with radiation, though more weakly.

## **Time-Dependent Perturbation Theory Gives the Selection Rules for Transitions**

Spectroscopic selection rules decide which transitions between quantum mechanical states are the most intense.

Until now, we have been considering wave functions obtained by solving the **time-independent Schrödinger equation for stationary states of isolated atoms and molecules**

$$\hat{H}\psi(\vec{r}) = E\psi(\vec{r})$$

But transitions from one state to another, as the terminology implies, are transient processes described by the **time-dependent Schrödinger equation**

$$\hat{H}\Psi(\vec{r}, t) = i\hbar \frac{\partial \Psi(\vec{r}, t)}{\partial t}$$

***Time-Dependent Perturbation Theory*** To solve this equation for spectroscopic transitions, the time-dependent part of the Hamiltonian operator  $\hat{H}^{(1)}$  is treated as a small perturbation superimposed on the time-independent Hamiltonian  $\hat{H}^{(0)}$  for isolated atoms and molecules in stationary states.

$$\hat{H}(\vec{r}, t) = \hat{H}^{(0)}(\vec{r}) + \hat{H}^{(1)}(\vec{r}, t)$$

To solve the time-dependent Schrödinger equation

$$(\hat{H}^{(0)} + \hat{H}^{(1)})\Psi(\vec{r}, t) = i\hbar \frac{\partial \Psi(\vec{r}, t)}{\partial t}$$

it's convenient to simplify the equations by assuming that the electric field of the electromagnetic radiation oscillates in the  $z$ -direction

$$E(t) = E_{0z} \cos(2\pi\nu t)$$

$\nu$  is the frequency of the radiation and  $E_{0z}$  is the amplitude of the oscillations in the electric field. If  $\mu_z$  is the dipole moment of a molecule in the  $z$ -direction, the energy of interaction between the radiation and the molecule is

$$\hat{H}^{(1)} = -\vec{\mu} \cdot \vec{E} = -\mu_z E_{0z} \cos(2\pi\nu t)$$

If the molecule has no dipole moment in the  $z$ -direction (no separation of charge, permanent or temporary, along the  $z$ -axis), there is no interaction.

**Transitions from State 1 to State 2** Consider possible transitions between stationary states 1 and 2 with wave functions  $\psi_1$  and  $\psi_2$  (note: *lower-case* psis!) satisfying the time-independent Schrödinger equations

$$\hat{H}^{(0)}\psi_1(\vec{r}) = E_1\psi_1(\vec{r})$$

$$\hat{H}^{(0)}\psi_2(\vec{r}) = E_2\psi_2(\vec{r})$$

$\hat{H}^{(0)}$  for the stationary states does not depend on the time. As a result, it's relatively easy to show (*try it!*) that the corresponding wave functions (*upper-case* psis!)

$$\Psi_1(\vec{r}, t) = \psi_1(\vec{r}) e^{-iE_1 t / \hbar}$$

$$\Psi_2(\vec{r}, t) = \psi_2(\vec{r}) e^{-iE_2 t / \hbar}$$

are solutions of the time-dependent Schrödinger equations

$$\hat{H}^{(0)} \Psi_1(\vec{r}, t) = i\hbar \frac{\partial \Psi_1(\vec{r}, t)}{\partial t}$$

$$\hat{H}^{(0)} \Psi_2(\vec{r}, t) = i\hbar \frac{\partial \Psi_2(\vec{r}, t)}{\partial t}$$

Suppose that the system is initially in state 1, and the perturbation (the applied radiation field) is “**turned on**” at time  $t = 0$ . The subsequent time-evolution of the state of the molecule is then represented by the linear combinations of states 1 and 2

$$\Psi(\vec{r}, t) = a_1(t) \Psi_1(\vec{r}, t) + a_2(t) \Psi_2(\vec{r}, t)$$

with time-dependent mixing coefficients  $a_1(t)$  and  $a_2(t)$  to be determined. The system is initially in state 1, so the initial conditions are

$$a_1(0) = 1 \qquad a_2(0) = 0$$

Substituting the expression for  $\Psi(\vec{r}, t)$  into

$$(\hat{H}^{(0)} + \hat{H}^{(1)})\Psi(\vec{r}, t) = i\hbar \frac{\partial \Psi(\vec{r}, t)}{\partial t}$$

gives the rather complicated expression

$$\begin{aligned} a_1(t)\hat{H}^{(0)}\Psi_1 + a_2(t)\hat{H}^{(0)}\Psi_2 + a_1(t)\hat{H}^{(1)}\Psi_1 + a_2(t)\hat{H}^{(1)}\Psi_2 \\ = i\hbar\Psi_1 \frac{d a_1(t)}{d t} + i\hbar\Psi_2 \frac{d a_2(t)}{d t} + i\hbar a_1(t) \frac{\partial \Psi_1(\vec{r}, t)}{\partial t} + i\hbar a_2(t) \frac{\partial \Psi_2(\vec{r}, t)}{\partial t} \end{aligned}$$

**But wait!** The first two terms and the last two terms in this equation cancel (*why?*) to give

$$a_1(t)\hat{H}^{(1)}\Psi_1 + a_2(t)\hat{H}^{(1)}\Psi_2 = i\hbar\Psi_1 \frac{d a_1(t)}{d t} + i\hbar\Psi_2 \frac{d a_2(t)}{d t}$$

This equation can be multiplied by  $\Psi_2^*$  and integrated over the spatial coordinates  $\tau$



$$\begin{aligned}
& a_1(t) \int \Psi_2^* \hat{H}^{(1)} \Psi_1 \, d\tau + a_2(t) \int \Psi_2^* \hat{H}^{(1)} \Psi_2 \, d\tau \\
&= i\hbar \frac{da_1(t)}{dt} \int \Psi_2^* \Psi_1 \, d\tau + i\hbar \frac{da_2(t)}{dt} \int \Psi_2^* \Psi_2 \, d\tau
\end{aligned}$$

$\Psi_1$  and  $\Psi_2$  are normalized and orthogonal (“orthonormal”), and so

$$a_1(t) \int \Psi_2^* \hat{H}^{(1)} \Psi_1 \, d\tau + a_2(t) \int \Psi_2^* \hat{H}^{(1)} \Psi_2 \, d\tau = i\hbar \frac{da_2(t)}{dt}$$

Substituting the spatial ( $\psi_i$ ) and time-dependent ( $e^{-iE_i t/\hbar}$ ) factors for  $\Psi_1$  and  $\Psi_2$

$$\begin{aligned}
& a_1(t) \int (\psi_2 e^{-iE_2 t/\hbar})^* \hat{H}^{(1)} \psi_1 e^{-iE_1 t/\hbar} \, d\tau \\
&+ a_2(t) \int (\psi_2 e^{-iE_2 t/\hbar})^* \hat{H}^{(1)} \psi_2 e^{-iE_2 t/\hbar} \, d\tau = i\hbar \frac{da_2}{dt}
\end{aligned}$$

leads to further simplification

$$a_1(t) e^{-i(E_1 - E_2)t/\hbar} \int \psi_2^* \hat{H}^{(1)} \psi_1 \, d\tau + a_2(t) \int \psi_2^* \hat{H}^{(1)} \psi_2 \, d\tau = i\hbar \frac{da_2}{dt}$$

For weak perturbations, relatively few atoms or molecules make the transition out of

the initial  $\Psi_1$  state. The term proportional to  $a_2(t)$  can therefore be neglected, at least initially, but *not* the term proportional to  $da_2/dt$  (*why?*), to give

$$e^{-i(E_1-E_2)t/\hbar} \int \psi_2^* \hat{H}^{(1)} \psi_1 d\tau = i\hbar \frac{da_2}{dt}$$

The derivative  $da_2/dt$  is especially interesting for spectroscopy. It gives the rate at which the population of molecules in state  $\Psi_2$  builds up as a result of the transition from the initial state  $\Psi_1$ .

The time-dependent perturbation Hamiltonian  $\hat{H}^{(1)}$  is proportional to the product of the electric dipole moment and the oscillating electric field (assumed for convenience to be along the  $z$  axis)

$$\hat{H}^{(1)} = -\mu_z E_{0z} \cos(2\pi\nu t) = -\mu_z E_{0z} (e^{i2\pi\nu t} + e^{-i2\pi\nu t})$$

So the expression for  $da_2/dt$  becomes

$$\begin{aligned} i\hbar \frac{da_2}{dt} &= -e^{-i(E_1-E_2)t/\hbar} \int \psi_2^* \mu_z E_{0z} (e^{i2\pi\nu t} + e^{-i2\pi\nu t}) \psi_1 d\tau \\ &= -(e^{-i(E_1-E_2-h\nu)t/\hbar} + e^{-i(E_1-E_2+h\nu)t/\hbar}) E_{0z} \int \psi_2^* \mu_z \psi_1 d\tau \end{aligned}$$

Defining the **dipole transition moment between states  $\Psi_1$  and  $\Psi_2$**

$$(\mu_z)_{21} = \int \psi_2^* \mu_z \psi_1 d\tau$$

we find

$$\frac{da_2}{dt} \propto E_{0z}(\mu_z)_{21} (e^{-i(E_1-E_2-h\nu)t/\hbar} + e^{-i(E_1-E_2+h\nu)t/\hbar})$$

Integrating between time  $t = 0$  (when  $a_2$  for the amplitude of the final state is zero) and time  $t$  gives

$$a_2(t) \propto E_{0z}(\mu_z)_{21} \left[ \frac{1 - e^{i(E_2-E_1+h\nu)t/\hbar}}{E_2 - E_1 + h\nu} + \frac{1 - e^{i(E_2-E_1-h\nu)t/\hbar}}{E_2 - E_1 - h\nu} \right]$$

**Why bother to do all this?** The results are fundamental and important:

1. For **absorption spectroscopy** (the final state has higher energy,  $E_2 > E_1$ ) the important **resonance denominator**  $E_2 - E_1 - h\nu$  causes the second term to be relatively large determining  $a_2(t)$  when

$$E_2 - E_1 = \Delta E = h\nu \quad \text{absorption}$$

For **emission spectroscopy** (the final state has lower energy,  $E_2 < E_1$ ) the **resonance denominator**  $E_2 - E_1 + h\nu$  causes the first term to be relatively large when

$$E_1 - E_2 = \Delta E = h\nu \quad \text{emission}$$

This is the famous **Bohr frequency condition**:

*When a system makes a transition from one state to another, it absorbs (or emits) a photon whose energy is equal to the difference in the energies of the two states.*

2. There is no absorption or emission if the dipole transition moment (decided by the stationary initial and final states) is zero.
  
3. The strength of the absorption is proportional to the dipole transition moment and the amplitude of the oscillating electric field.

### Application to the Spectroscopic Selection Rules for Diatomic Rigid Rotors

The time-dependent perturbation theory of spectroscopic transitions combined with the properties of spherical harmonics can be used to derive the selection rules for **linear rigid rotors**. These rules give the observed rotational spectra of diatomics and other molecules.

From last term, the wave functions for rigid rotors are spherical harmonics  $Y_J^M(\theta, \phi)$

$$\hat{H}Y_J^M(\theta, \phi) = E_J Y_J^M(\theta, \phi)$$

with rotational energies

$$E_J = \frac{J(J+1)\hbar^2}{2I} \quad J = 0, 1, 2, 3, \dots$$

$I$  is the moment of inertia

$$I = \frac{m_1 m_2}{m_1 + m_2} r^2$$

Spherical harmonic functions are also eigenfunctions of the operator for the square of angular momentum

$$\hat{L}^2 Y_J^M(\theta, \phi) = \hbar^2 J(J+1) Y_J^M(\theta, \phi)$$

and the operator for the  $z$ -component of the angular momentum

$$\hat{L}_z Y_J^M(\theta, \phi) = \hbar M Y_J^M(\theta, \phi)$$

with respective eigenvalues  $\hbar^2 J(J+1)$  and  $\hbar M$ . The energy of the rotor and the corresponding squared angular momentum differ only by a factor of  $1/2$  (**why?**).

### ***But what about the spectroscopy?***

To see if transitions between different rotational states are allowed (*i.e.*, probable), time-dependent perturbation theory suggests that we look at the dipole transition moment between the different states

$$M', J' \rightarrow M, J$$

Using  $\mu_z = \mu \cos \theta$ , we get

$$\begin{aligned}
 (\mu_z)_{JM, J'M'} &= \iint Y_{J'}^{M'}(\theta, \phi) * \hat{\mu} Y_J^M(\theta, \phi) \sin \theta d\theta d\phi \\
 &= \mu \iint Y_{J'}^{M'}(\theta, \phi) * Y_J^M(\theta, \phi) \sin \theta \cos \theta d\theta d\phi
 \end{aligned}$$

Notice that the dipole moment must be nonzero for the transition moment to be nonzero. So, according to the rigid rotor model:

Rule #1. **A diatomic must have a permanent dipole to have a rotational spectrum.**

**Why?** It is instructive to think about what happens when a diatomic molecule is placed in an electric field (assumed to be in the  $z$ -direction).

To generate an energy change, and therefore an interaction between the electric field and the molecule, there must be a separation of charge along the  $z$  axis.

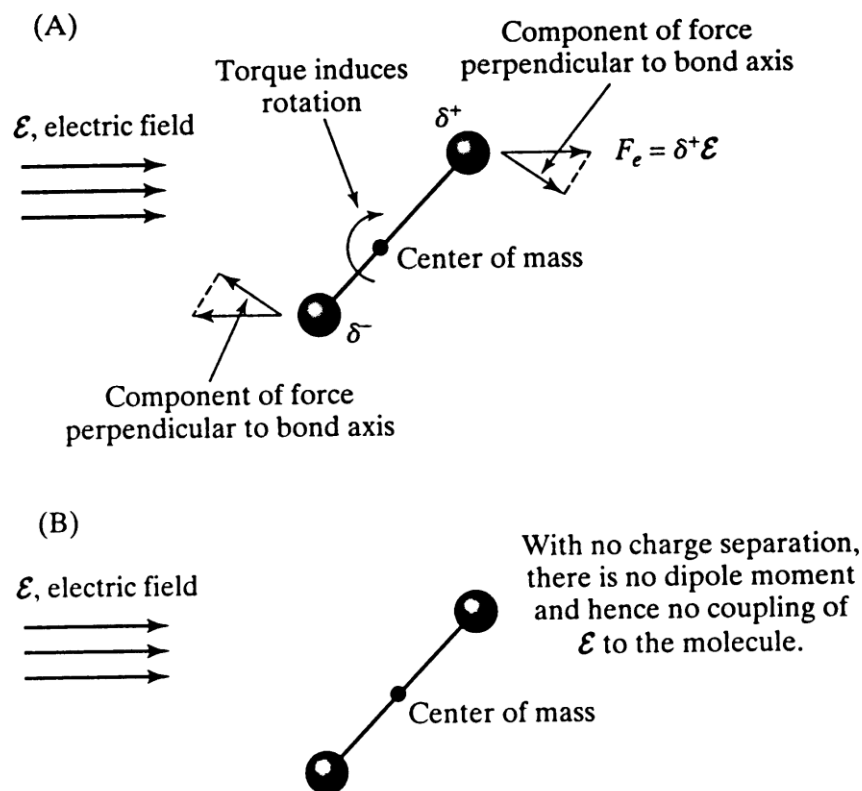
$$\text{electric potential energy} = -\vec{\mu} \cdot \vec{E}$$

Why is there a minus sign? The electric field is defined as the negative gradient in the electric potential. It gives the direction in which a mobile positive charge would move.

$$\vec{E} = -\nabla \phi$$

So a positive electric field combined with a positive dipole has negative potential energy.

## Interaction of an Electric Field with a Diatomic Molecule



Next we ask: for what values of the quantum numbers  $M'$ ,  $J'$ ,  $M$ ,  $J$  is the transition moment nonzero? From our treatment of a three-dimensional rotor

$$Y_J^M(\theta, \phi) = N_{M,J} P_J^{|M|}(\cos\theta) e^{iM\phi}$$

where  $N_{M,J}$  is a normalization constant and  $P_J^{|M|}(\cos\theta)$  is a Legendre function. Letting  $x = \cos\theta$  and noting that  $dx = -\sin\theta d\theta$ , the expression for the transition moment dipole becomes

$$(\mu_z)_{JM, J'M'} = \mu N_{J'M'} N_{JM} \int_0^{2\pi} e^{i(M-M')\phi} d\phi \int_{-1}^1 x P_{J'}^{|M'|}(x) P_J^{|M|}(x) dx$$

The integral in  $\phi$  vanishes unless  $M = M'$ . This condition gives selection rule #2:

**#2.  $\Delta M = 0$**

**Why?** Notice from the diagram above that the electric field exerts a twisting force (torque) on the molecule affecting its rotation in a plane *parallel to the z axis*, so there is no change in the z-angular momentum (*rotation perpendicular to the z-axis*).

Integration over  $\phi$  for  $M = M'$  gives a factor of  $2\pi$ :

$$(\mu_z)_{JM, J'M'} = 2\pi\mu N_{J'M'} N_{JM} \int_{-1}^1 P_{J'}^{|M'|}(x) x P_J^{|M|}(x) dx$$

To complete the selection rules for diatomics, we can substitute result from the recursion rule for Legendre functions

$$(2J+1)xP_J^{|M|}(x) = (J-|M|+1)P_{J+1}^{|M|}(x) + (J+|M|)P_{J-1}^{|M|}(x)$$

into the integral for the transition dipole moment to get

$$(\mu_z)_{JM, J'M} = 2\pi\mu N_{J'M} N_{JM} \int_{-1}^1 \left[ \frac{J-|M|+1}{2J+1} P_{J+1}^{|M|} + \frac{J+|M|}{2J+1} P_{J-1}^{|M|} \right] P_{J'}^{|M|}(x) dx$$



The  $P_J^{|M|}(x)$  functions are orthonormal, so integrals over  $P_{J+1}^{|M|}(x) P_J^{|M|}(x)$  and  $P_{J-1}^{|M|}(x) P_J^{|M|}(x)$  will be nonzero only if  $J' = J + 1$  or  $J' = J - 1$ , respectively. This result gives the final selection rule for the rotational transitions for diatomics:

$$\boxed{\#3. \quad \Delta J = \pm 1}$$

**Why?** Photons (spin 1) have angular momentum too!  $\Delta J = 1$  corresponds to the absorption of a photon and  $\Delta J = -1$  corresponds to emission of a photon.

## Rotational Spectra of Polyatomic Molecules

Up to now, only the rotation of diatomic molecules has been analyzed. In general, the rotation of any molecule can be expressed in terms of the moments of inertia about any three perpendicular axes.

$$I = \sum_{i=1}^N m_i r_i^2$$

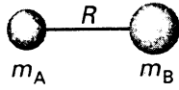
This sum over all  $N$  nuclei with masses  $m_i$  at a distance  $r_i$  from the axis of rotation.

The convention is to label the three moments of inertia  $I_a$ ,  $I_b$ , and  $I_c$  with the axes chosen so that  $I_c \geq I_b \geq I_a$ .

# Molecular Moments of Inertia

( $m$  is the total mass of the molecule)

## 1. Diatomics

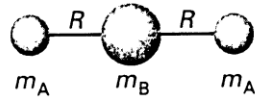


$$I = \frac{m_A m_B}{m} R^2 = \mu R^2$$

## 2. Linear rotors

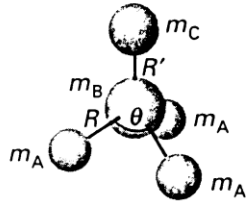


$$I = m_A R^2 + m_C R'^2 + \frac{(m_A R - m_C R')^2}{m}$$



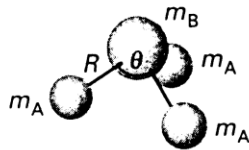
$$I = 2m_A R^2$$

## 3. Symmetric rotors



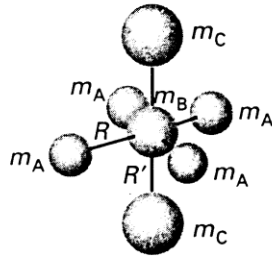
$$I_{\parallel} = 2m_A R^2 (1 - \cos \theta)$$

$$I_{\perp} = m_A R^2 (1 - \cos \theta) + \frac{m_A}{m} (m_B + m_C) R^2 (1 + 2 \cos \theta) + \frac{m_C R'}{m} \{ (3m_A + m_B) R' + 6m_A R [\frac{1}{3} (1 + 2 \cos \theta)]^{1/2} \}$$



$$I_{\parallel} = 2m_A R^2 (1 - \cos \theta)$$

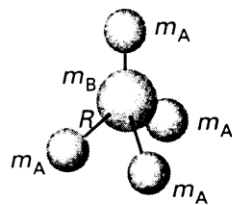
$$I_{\perp} = m_A R^2 (1 - \cos \theta) + \frac{m_A m_B}{m} R^2 (1 + 2 \cos \theta)$$



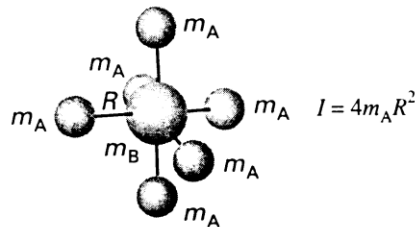
$$I_{\parallel} = 4m_A R^2$$

$$I_{\perp} = 2m_A R^2 + 2m_C R'^2$$

## 4. Spherical rotors



$$I = \frac{8}{3} m_A R^2$$



$$I = 4m_A R^2$$

## Diatomics and Linear Rotors

Linear molecules (*e.g.*, HCl, CO<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>) have all nuclei on a single axis. In this case the moment of inertia around the bond axis is zero and

$$I_c = I_b = I$$

$$I_a = 0$$

$$E_J = \frac{L^2}{2I} = \frac{J(J+1)\hbar^2}{2I} \quad J = 0, 1, 2, 3, 4,$$

$$E_J = 0, \quad \frac{\hbar^2}{I}, \quad \frac{3\hbar^2}{I}, \quad \frac{6\hbar^2}{I}, \quad \dots \quad (\text{the energy difference increases with } J)$$

The energy of a photon ( $h\nu$ ) is proportional to its frequency. And because  $1/\lambda = \nu/c$ , dividing a frequency by the speed of light gives wavenumbers. Historically, spectroscopists are fond of expressing energies in these units:

$$\tilde{E}_J = \frac{E_J}{hc} = \frac{J(J+1)\hbar^2}{2Ihc} = \frac{J(J+1)\hbar}{4\pi cI}$$

The quantity

$$B = \frac{\hbar}{4\pi cI}$$

is called the **rotational constant** of a molecule. It provides the convenient expression

$$\tilde{E}_J = BJ(J+1)$$

for rotational energies in wavenumbers.

## Spherical Rotors

Molecules such as CH<sub>4</sub> and SF<sub>6</sub> have **three identical moments of inertia**.

$$I_a = I_b = I_c = I$$

$$E_J = \frac{L^2}{2I} = \frac{J(J+1)\hbar^2}{2I} \quad J = 0, 1, 2, 3, 4,$$

$$\tilde{E}_J = BJ(J+1)$$

$$B = \frac{\hbar}{4\pi cI}$$

## Symmetric Rotors

In symmetric rotors, two moments of inertia are identical, but different from the third moment of inertia, as for CH<sub>3</sub>Cl, NH<sub>3</sub>, C<sub>6</sub>H<sub>6</sub>.

The unique axis of the molecule is called the **principal axis** and designated by  $I_{\parallel}$ . The two equivalent moments of inertia are designated by  $I_{\perp}$ .

**Prolate symmetric rotors** (e.g., CH<sub>3</sub>Cl) have  $I_{\parallel} < I_{\perp}$ .  $(I_c = I_b = I_{\perp}, I_a = I_{\parallel})$   
(like footballs)

**Oblate symmetric rotors** (e.g., C<sub>6</sub>H<sub>6</sub>) have  $I_{\parallel} > I_{\perp}$ .  $(I_c = I_{\parallel}, I_b = I_a = I_{\perp})$   
(like pancakes)

The rotational energy in this case is the sum of the angular momentum for each axis divided by twice the moment of inertia.

For prolate rotors ( $I_c = I_b$ )

$$E = \frac{L_c^2 + L_b^2}{2I_{\perp}} + \frac{L_a^2}{2I_{\parallel}}$$

The total angular momentum is  $L^2 = L_a^2 + L_b^2 + L_c^2$ , and so

$$E = \frac{L^2 - L_a^2}{2I_{\perp}} + \frac{L_a^2}{2I_{\parallel}} = \frac{L^2}{2I_{\perp}} + L_a^2 \left( \frac{1}{2I_{\parallel}} - \frac{1}{2I_{\perp}} \right)$$

From the quantum mechanics of rotation motion, we know that the total angular momentum squared can have the values

$$L^2 = J(J+1)\hbar^2 \quad J = 0, 1, 2, 3, 4,$$

We also know that the angular momentum for any particular axis (say the  $a$ -axis) is restricted to the values

$$L_a = K\hbar \quad K = 0, \pm 1, \pm 2, \pm 3, \dots, \pm J$$

These considerations give the energy levels

$$E = \frac{J(J+1)^2 \hbar^2}{2I_{\perp}} + \left( \frac{1}{2I_{\parallel}} - \frac{1}{2I_{\perp}} \right) K^2 \hbar^2$$

$$\tilde{E}_{J,K} = BJ(J+1) + (A-B)K^2$$

and the rotational constants

$$A = \frac{\hbar}{4\pi c I_{||}} \qquad B = \frac{\hbar}{4\pi c I_{\perp}}$$

In cases where  $K = 0$ , there is no angular momentum about the principal axis, and the energy levels depends only on  $I_{\perp}$ . When  $K = \pm J$ , most of the angular momentum arises from rotation around the principal axis. Notice that the sign of  $K$  does not affect the energy. The sign of  $K$  indicates the direction of rotation, clockwise or counterclockwise, which does not change the energy.

### Selection Rules for Rotational Spectra of Polyatomic Molecules

For a molecule to have allowed transitions between different rotational states, it must have a permanent dipole moment. This means that homonuclear diatomics (such as O=O), symmetrical linear molecules (such as O=C=O), and spherical rotors (such as CH<sub>4</sub>) cannot have rotational spectra.

For unsymmetrical linear molecules (such as C=O), the selection rules  $\Delta J = \pm 1$  and  $\Delta M = 0$  derived previously apply.

For symmetric rotors (such as NH<sub>3</sub>), we have  $\Delta J = \pm 1$  and  $\Delta K = 0$ . Any dipole moment possessed by a symmetric rotor must lie along the principal axis. Such a molecule cannot be accelerated into different rotational energy levels about this axis by the absorption of radiation. A dipole moment perpendicular to the principal axis would be required to do this.

**But ...** In practice, using long-path length absorption cells, weak “forbidden” rotational transitions (e.g., for SiH<sub>4</sub>) can be observed. **Why?**

## Spectroscopic Selection Rules: Diatomic Harmonic Oscillators

To illustrate the selection rules for **molecular vibration**, we can apply time-dependent perturbation theory to the diatomic harmonic oscillator.

Recall that the **harmonic oscillator wave functions** are

$$\psi_n(q) = N_n H_n(\alpha^{1/2}q) e^{-\alpha q^2/2} \quad n = 0, 1, 2, 3, \dots$$

$N_n$  is a normalization factor,  **$q$  is the displacement** of the positions of nuclei 1 and 2 from the equilibrium bond length  $R_0$  (stretched:  $q > 0$ , compressed:  $q < 0$ )

$$q = z_2 - z_1 - R_0$$

and  $\alpha$  is an abbreviation for

$$\alpha = \sqrt{k\mu/\hbar^2}$$

$k$  is the force constant (a measure of the “stiffness” of the bond),  $\mu$  is the reduced mass.

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

and  $H_n(\alpha^{1/2}q)$  is the  $n$ th **Hermite polynomial**.

$$H_0(\xi) = 1 \quad (\text{even})$$

$$H_1(\xi) = 2\xi \quad (\text{odd})$$

$$H_2(\xi) = 4\xi^2 - 2 \quad (\text{even})$$

$$H_3(\xi) = 8\xi^3 - 12\xi \quad (\text{odd})$$

$$H_4(\xi) = 16\xi^4 - 48\xi^2 + 12 \quad (\text{even})$$

$$H_5(\xi) = 32\xi^5 - 160\xi^3 + 120\xi \quad (\text{odd})$$

*Etc.*

The energy levels for a harmonic oscillator are equally spaced

$$E_n = \hbar \sqrt{\frac{k}{\mu}} \left( n + \frac{1}{2} \right) \quad n = 0, 1, 2, 3, \dots$$

with  $E_{n+1} - E_n = \Delta E = (h/2\pi)(k/\mu)^{1/2}$ .

Experiments show that homonuclear diatomics, such as N<sub>2</sub>, have no vibrational spectra of significant intensity. For heteronuclear diatomics, such as NO, only one relatively intense vibrational frequency (called the **fundamental frequency**) is observed:

$$\nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$



**Why?** Shouldn't there be an infinite number of  $n \leftrightarrow n'$  transitions  $1 \leftrightarrow 2, 1 \leftrightarrow 3, 1 \leftrightarrow 4, \dots, 2 \leftrightarrow 3, 2 \leftrightarrow 4, 2 \leftrightarrow 5, \dots$  with frequencies  $\nu_0, 2\nu_0, 3\nu_0, 4\nu_0, \dots$ ?

To see if transitions between different vibrational states are allowed (*i.e.*, probable), time-dependent perturbation theory suggests that we look at the dipole transition moment  $(\mu_z)_{n,n'}$  between the different vibrational states

$$n \rightarrow n' \quad \text{transition}$$

The degree of charge separation, and therefore the dipole moment along the bond axis (assumed to be the  $z$ -axis), can change as the bond length oscillates, so the dipole moment, in general, is a function of  $q$  (the deviation from the equilibrium bond length).

$$\begin{aligned} (\mu_z)_{n,n'} &= \int \psi_{n'}^*(q) \mu(q) \psi_n(q) \mathrm{d}q \\ &= \int N_{n'} H_{n'}(\alpha^{1/2} q) e^{-\alpha q^2/2} \mu(q) N_n H_n(\alpha^{1/2} q) e^{-\alpha q^2/2} \mathrm{d}q \end{aligned}$$

The dipole moment can be expanded in a Taylor series about the value  $\mu_0$  at the equilibrium bond length ( $q = 0$ )

$$\mu_z(q) = \mu_0 + \left( \frac{\mathrm{d}\mu}{\mathrm{d}q} \right)_0 q$$

to give

$$(\mu_z)_{n,n'} = \int N_{n'} H_{n'}(\alpha^{1/2} q) \left( \mu_0 + \frac{d\mu}{dq} q \right) N_n H_n(\alpha^{1/2} q) e^{-\alpha q^2} dq$$

which is equivalent to the two integrals

$$\begin{aligned} (\mu_z)_{n,n'} &= N_{n'} N_n \mu_0 \int H_{n'}(\alpha^{1/2} q) H_n(\alpha^{1/2} q) e^{-\alpha q^2} dq \\ &\quad + N_{n'} N_n \frac{d\mu}{dq} \int H_{n'}(\alpha^{1/2} q) q H_n(\alpha^{1/2} q) e^{-\alpha q^2} dq \end{aligned}$$

Because wave functions for the harmonic oscillator are orthogonal, the first integral is zero. To evaluate the second integral, the recursion formula for Hermite polynomials

$$\xi H_n(\xi) = n H_{n-1}(\xi) + \frac{1}{2} H_{n+1}(\xi)$$

is helpful. Defining  $\xi = \alpha^{1/2} q$  gives ( $\xi$  is the Greek letter xi, not to be confused with  $\zeta$ , the Greek letter zeta!)

$$(\mu_z)_{n,n'} = \frac{N_{n'} N_n}{\alpha} \left( \frac{d\mu}{dq} \right)_0 \int H_{n'}(\xi) \left[ n H_{n-1}(\xi) + \frac{1}{2} H_{n+1}(\xi) \right] e^{-\xi^2} dq$$

The Hermite polynomials are orthogonal, so the dipole transition moment is zero unless

$$n' = n - 1 \qquad \text{or} \qquad n' = n + 1$$

This gives the important selection rule for the allowed transitions for the harmonic oscillator:

**Rule #1.**       $\Delta n = \pm 1$

In addition, the factor  $(d\mu/dq)_0$  in the expression for the dipole transition moment gives

**Rule #2.**      **The dipole moment of the molecule must vary during a vibration.**

Can you use the second rule to understand why homonuclear diatomics are infrared inactive? Does this mean homonuclear diatomics are not vibrating?

Carbon dioxide (O=C=O) has no permanent dipole, but it is strongly infrared active. (Go ask the environmentalists). Why?

Transitions with  $\Delta n = \pm 2$  (called **overtones**), forbidden by rule #1, are in fact routinely observed, though relatively weak in intensity. Can you explain this? Is quantum mechanics wrong?

### Vibration of Polyatomic Molecules

So far we have only considered the vibration of diatomic molecules. The vibration of polyatomic molecules (such as H<sub>2</sub>O, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>6</sub>H<sub>6</sub>) is more complicated, but it can be easily understood using the harmonic oscillator approximation and the concept of **normal coordinates**.

Consider a molecule containing  $N$  nuclei (*e.g.*,  $N = 5$  for CH<sub>4</sub>). A complete description of the motion of the molecule in three-dimensional space requires the specification of three velocity components  $v_x$ ,  $v_y$ ,  $v_z$  for each of the  $N$  nuclei, for a total of  $3N$  velocity variables, which are often called **degrees of freedom**.

Of the  $3N$  total degrees of freedom, three are used to specify the motion of the center of mass of the molecule through space. These three coordinates are called **translational degrees of freedom**.

For **linear molecules** (such as  $N_2$  or  $CO_2$ ), with **all nuclei on a single axis**, there are two rotational axes, and therefore **two rotational degrees of freedom**.

**Nonlinear molecules** (such as  $H_2O$  or  $CH_4$ ) have three rotational axes and therefore **three rotational degrees of freedom**.

The coordinates remaining, after translation and rotation are specified, must describe the vibrational motion of the nuclei, so

**linear molecules**                     $3N - 3 - 2 = 3N - 5$  **vibrational degrees of freedom**

**nonlinear molecules**             $3N - 3 - 3 = 3N - 6$  **vibrational degrees of freedom**

### Examples of Degrees of Freedom

Molecule	Total	Translational	Rotational	Vibrational
HCl	6	3	2	1
O=C=O	9	3	2	4
H <sub>2</sub> O	9	3	3	3
NH <sub>3</sub>	12	3	3	6
CH <sub>4</sub>	15	3	3	9

The potential energy of a vibrating molecule is a function of the  $N_{\text{vib}} = 3N - 5$  (for linear molecules) or  $3N - 6$  (for nonlinear molecules) vibrational coordinates. If the displacements from the equilibrium values of these coordinates (no compression and no stretching) are denoted by

$$q_1, q_2, q_3, \dots, q_{N_{\text{vib}}}$$

For a single harmonic vibration, Hooke's law states that the restoring force

$$F = -kq$$

is proportional to the displacement  $q$  with force constant  $k$ . Integration of  $-Fdq = kq dq$  gives the potential energy

$$\text{potential energy} = \frac{1}{2} kq^2$$

Extending these ideas to a polyatomic molecule with  $N_{\text{vib}}$  vibrational degrees of freedom gives the expression

$$V(q_1, q_2, \dots, q_{N_{\text{vib}}}) = \frac{1}{2} \sum_{i=1}^{N_{\text{vib}}} \sum_{j=1}^{N_{\text{vib}}} \frac{\partial^2 V}{\partial q_i \partial q_j} q_i q_j = \frac{1}{2} \sum_{i=1}^{N_{\text{vib}}} \sum_{j=1}^{N_{\text{vib}}} k_{ij} q_i q_j$$

for the potential energy with force constants  $k_{ij}$ .

Cross-terms such as  $k_{12}$ ,  $k_{32}$ , *etc.* representing interactions between the vibrations make it very difficult to solve Schrödinger's equation for polyatomic vibration.

Using an ingenious mathematical procedure based on matrix diagonalization and eigenvalues, we can transform from the  $q_i$  coordinates to a new set of **normal coordinates**  $Q_i$  that diagonalize the matrix of force constants to give

$$V(Q_1, Q_2, \dots, Q_{N_{\text{vib}}}) = \frac{1}{2} \sum_{i=1}^{N_{\text{vib}}} K_i Q_i^2$$

In terms of normal coordinates, the Hamiltonian operators for the normal vibrations are

$$\hat{H}_{\text{vib},i} = -\frac{\hbar^2}{2\mu_i} \frac{d^2}{dQ_i^2} + \frac{1}{2} \sum_{i=1}^{N_{\text{vib}}} K_i Q_i^2$$

We have already solved Schrödinger's equation for this operator! For the  $i$ th vibration, the energy levels are

$$E_n^{(i)} = \left(n_i + \frac{1}{2}\right) h\nu_i \quad n = 0, 1, 2, 3, \dots$$

where  $\nu_i$  is the fundamental frequency for the  $i$ th normal vibration.

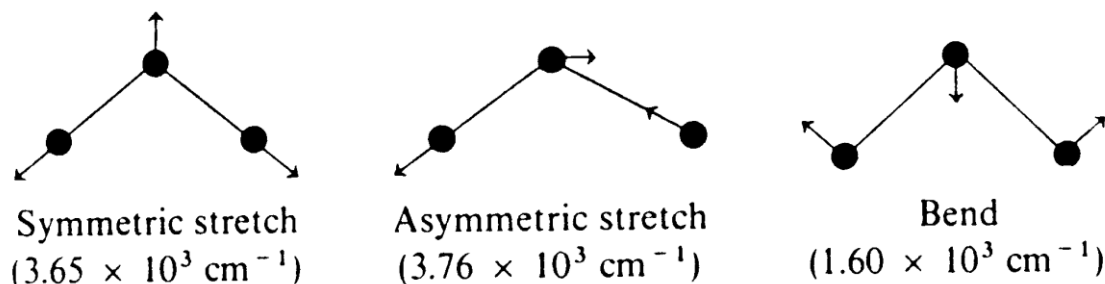
Summing over all of the normal vibrations give the total vibrational energy for a polyatomic molecule:

$$E_{\text{vib}} = \sum_{i=1}^{N_{\text{vib}}} \left(n_i + \frac{1}{2}\right) h\nu_i$$

**This result is important because it means that under the harmonic oscillator approximation, the vibrational motion of a polyatomic molecule can be represented as the sum of  $N_{\text{vib}}$  independent vibrations, each with a characteristic fundamental frequency.**

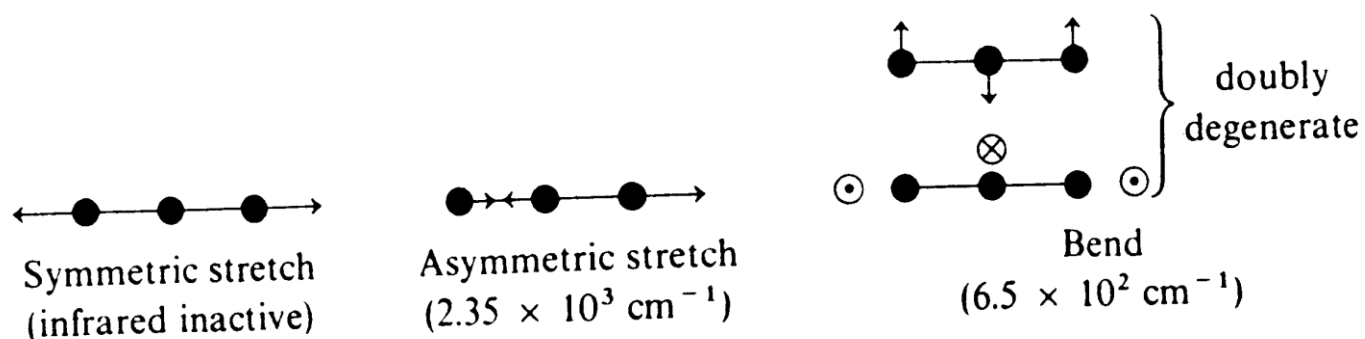
## H<sub>2</sub>O

A water molecule has three degrees of vibrational freedom. The normal modes are:



## CO<sub>2</sub>

A carbon dioxide molecule has four degrees of vibrational freedom. The normal modes are:



There is no change in the dipole moment during the symmetric stretch, so it is infrared inactive. The asymmetric stretch and the two bending modes produce oscillating dipoles, so they are infrared active. The two bending modes are degenerate. As a result, CO<sub>2</sub> has only two fundamental lines in its infrared spectrum although there are four normal modes.

## Rotational-Vibrational Spectra for Diatomics

It is important to realize that the rigid rotor and harmonic oscillator are models that only approximately represent real diatomic models. Using measured transition frequencies, it is easy to measure departures from these models caused by

- ◆ anharmonicity (deviations from Hooke's law)
- ◆ centrifugal stretching (bond lengths increase slightly with  $J$ )
- ◆ vibration-rotation coupling (vibration causes small changes in  $I$ )

Nevertheless, it is a good first approximation to assume that vibrational and rotational energies of diatomics are independent and given by the harmonic oscillator and rigid rotor equations

$$E_{n,J} = \left(n + \frac{1}{2}\right)h\nu_0 + BJ(J + 1)$$

With fundamental vibrational frequency

$$\nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

and rotational constant ( $I$  is the moment of inertia)

$$B = \frac{\hbar^2}{2I}$$



**Pure Rotational Spectra** Transitions between states with different rotational quantum numbers  $J$  but identical vibrational quantum numbers  $n$

$$n, J \rightarrow n, J' \quad (\Delta n = 0, \Delta J = \pm 1)$$

produce pure rotational spectra which are usually measured by microwave absorption spectroscopy.

For absorption ( $J' = J + 1$ ), the allowed **pure-rotation transitions**  $n, J \rightarrow n, J'$  for a rigid rotor are:

$$n, 0 \rightarrow n, 1 \quad \Delta E = B(1)(1+1) - B(0)(0+1) = 2B$$

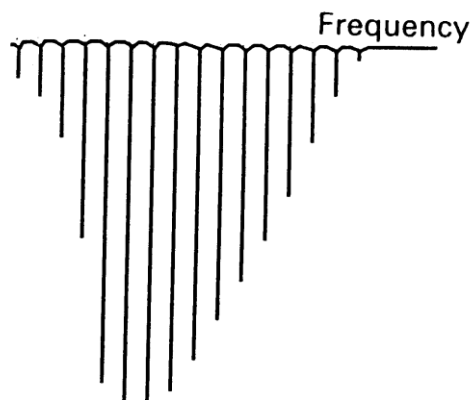
$$n, 1 \rightarrow n, 2 \quad \Delta E = B(2)(2+1) - B(1)(1+1) = 4B$$

$$n, 2 \rightarrow n, 3 \quad \Delta E = B(3)(3+1) - B(2)(2+1) = 6B$$

$$n, 3 \rightarrow n, 4 \quad \Delta E = B(4)(4+1) - B(3)(3+1) = 8B$$

*etc.*

The predicted spectra are series of **equally spaced absorption frequencies with spacing  $2B$** . The most intense transition corresponds to the rotational level  $J$  that is most highly populated according to the Boltzmann distribution law (more on that later).



**Rotational-Vibrational Spectra** Absorption of photons at higher frequencies (usually in the infrared) causes transitions between different vibrational and rotational levels.

$$n, J \rightarrow n + 1, J' \quad (\Delta n = 1, \Delta J = \pm 1)$$

The difference in vibrational energy in this case is  $(n + 1 + \frac{1}{2})h\nu_0 - (n + \frac{1}{2})h\nu_0 = h\nu_0$ .

Using  $E_{n,J} = (n + \frac{1}{2})h\nu_0 + BJ(J + 1)$ , we get:

The series of transitions with  $\Delta n = +1, \Delta J = +1$ , called the **R Branch**, occurs at the frequencies:

$$n, 0 \rightarrow n+1, 1 \quad \Delta E = h\nu_0 + B(1)(1+1) - B(0)(0+1) = h\nu_0 + 2B$$

$$n, 1 \rightarrow n+1, 2 \quad \Delta E = h\nu_0 + B(2)(2+1) - B(1)(1+1) = h\nu_0 + 4B$$

$$n, 2 \rightarrow n+1, 3 \quad \Delta E = h\nu_0 + B(3)(3+1) - B(2)(2+1) = h\nu_0 + 6B$$

$$n, 3 \rightarrow n+1, 4 \quad \Delta E = h\nu_0 + B(4)(4+1) - B(3)(3+1) = h\nu_0 + 8B$$

*etc.*

The series of transitions with  $\Delta n = +1, \Delta J = -1$ , called the **P Branch**, occurs at the lower frequencies:

$$n, 0 \rightarrow n+1, -1 \quad \text{not observed, states with } J = -1 \text{ do not exist}$$

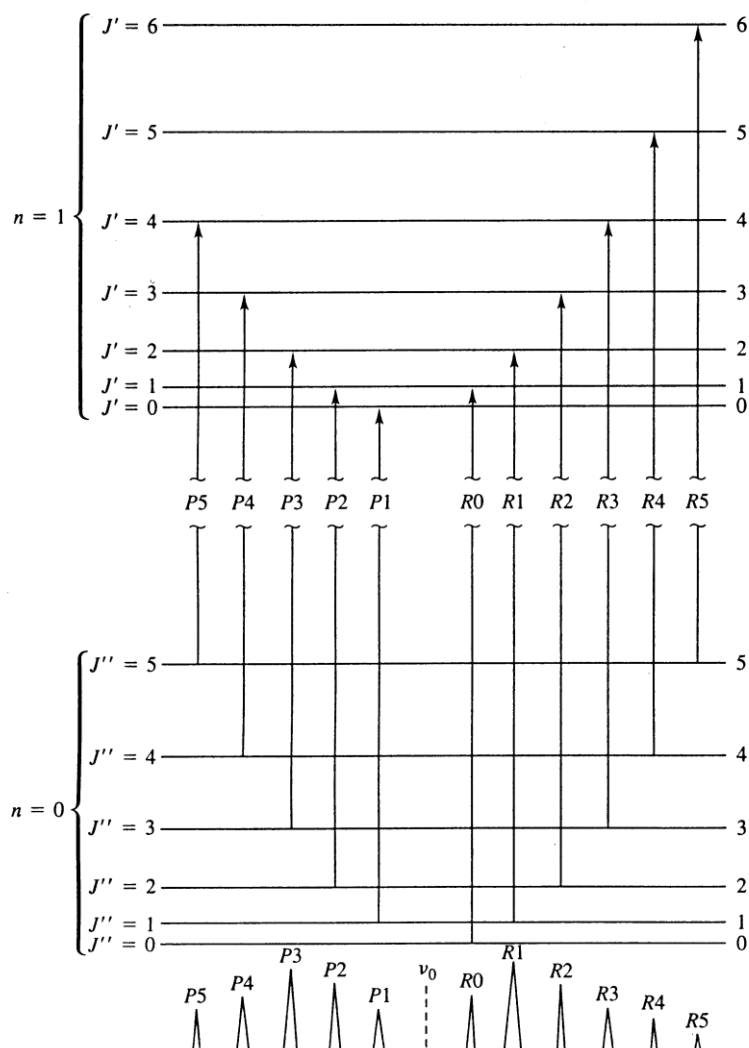
$$n, 1 \rightarrow n+1, 0 \quad \Delta E = h\nu_0 + B(0)(0+1) - B(1)(1+1) = h\nu_0 - 2B$$

$$n, 2 \rightarrow n+1, 1 \quad \Delta E = h\nu_0 + B(1)(1+1) - B(2)(2+1) = h\nu_0 - 4B$$

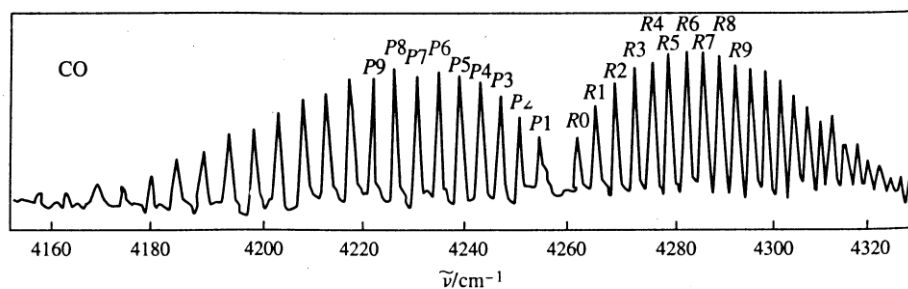
$$n, 3 \rightarrow n+1, 2 \quad \Delta E = h\nu_0 + B(2)(2+1) - B(3)(3+1) = h\nu_0 - 8B$$

*etc.*

## Rotational-Vibrational Transitions



## P and R Branches in the Infrared Spectrum of CO



There is a “gap” (missing line) near  $4260 \text{ cm}^{-1}$  because  $P_0$  ( $J = 0$  to  $J = -1$ ) and  $R_{-1}$  ( $J = -1$  to  $J = 0$ ) transitions are impossible. ( $J = -1$  is not a valid quantum number.)

## Analysis of High Resolution Rotational-Vibrational Spectra

The expression

$$E_{n,J} = \left(n + \frac{1}{2}\right)h\nu_0 + BJ(J + 1)$$

for the **energy levels of a combined rigid rotor and harmonic oscillator** is a good first approximation for the rotational-vibrational energies of diatomic molecules.

But with high resolution spectrometers, it is easy to measure deviations from the harmonic oscillator-rigid rotor model. These deviations provide useful additional information about molecules.

**Centrifugal Distortion** *Real molecules are not rigid rotors!* As the rotation rate increases, chemical bonds stretch slightly. The increase in bond length increases the moment of inertia and therefore decreases the spacing of the rotational energy levels. To account for this behavior, the term  $-DJ^2(J + 1)^2$  is added to the expression for the rotational energy levels to give

$$E_J = BJ(J + 1) - DJ^2(J + 1)^2$$

$D$  is the **centrifugal distortion constant**. Notice the minus sign in front of  $D$ .

For absorption:

$$\Delta E = E_{J+1} - E_J = 2B(J + 1) - 4D(J + 1)^3$$

For emission:

$$\Delta E = E_J - E_{J-1} = -2B(J + 1) + 4DJ^3$$

In practice, the frequencies and energy differences for spectroscopic transitions are often quoted in wavenumbers. A frequency  $\nu$  (in Hz) is converted to a frequency  $\tilde{\nu}$  in wavenumbers by dividing by the speed of light. An energy difference (in Joules) is converted to wavenumbers by dividing by  $hc$ .

$$\tilde{\nu} = \frac{\nu}{c} \qquad \Delta\tilde{E} = \frac{\Delta E}{hc}$$

### Rotational Absorption Spectrum of H<sup>35</sup>Cl

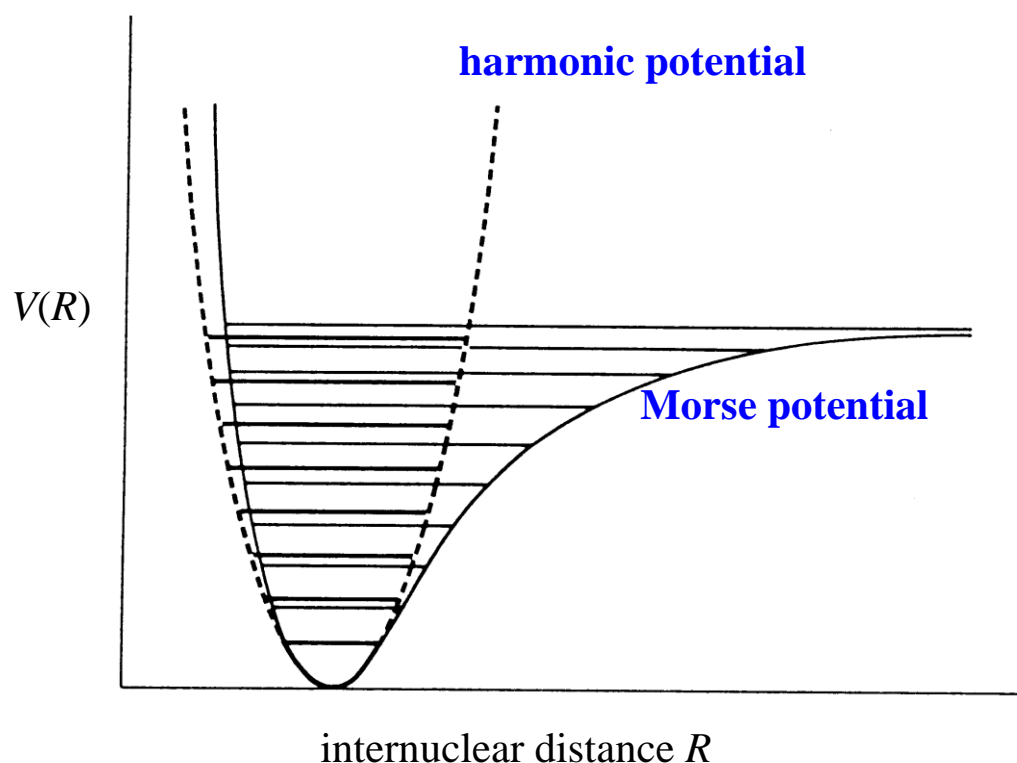
Transition	$\tilde{\nu}_{\text{obs}} / \text{cm}^{-1}$	$\Delta\tilde{\nu}_{\text{obs}} / \text{cm}^{-1}$	$\tilde{\nu}_{\text{calc}} = 2\tilde{B}J(J+1)$ $\tilde{B} = 10.34 \text{ cm}^{-1}$	$\tilde{\nu}_{\text{calc}} = 2\tilde{B}J(J+1) - 4D(J+1)^3$ $\tilde{B} = 10.395 \text{ cm}^{-1}$ $\tilde{D} = 0.0004 \text{ cm}^{-1}$
3 → 4	83.03		82.72	83.06
		21.07		
4 → 5	104.10		103.40	103.75
		20.20		
5 → 6	124.30		124.08	124.39
		20.73		
6 → 7	145.03		144.76	144.98
		20.48		
7 → 8	165.51		165.44	165.50
		20.35		
8 → 9	185.86		186.12	185.94
		20.52		
9 → 10	206.38		206.80	206.30
		20.12		
10 → 11	226.50		227.48	226.56
	rms deviations:		0.55	0.14

**Anharmonicity** The potential energy of a chemical bond passes through a minimum value at the equilibrium bond length  $R_0$ . Using a Taylor series expansion, the potential energy *near the minimum* is accurately represented by a Taylor series expansion truncated at the term in  $(R - R_0)^2$ .

$$V(R) = V(R_0) + \frac{dV}{dR}(R - R_0) + \frac{1}{2} \frac{d^2V}{dR^2}(R - R_0)^2 = V(R_0) + \frac{1}{2} k(R - R_0)^2$$

$dV/dR$  is zero in the expression (*why?*). The second derivative  $d^2V/dR^2$  at the minimum gives the force constant  $k$  for Hooke's Law.

But in general, **potential energy curves for chemical bonds are not parabolic functions of the bond length**. As the vibrational energy increases, the bond weakens. Eventually, the molecule shakes itself apart. The decrease in the force constant with increasing vibrational energy leads to a decrease in the spacing of the vibrational energy levels.



A more realistic potential energy curve over the whole range of  $R$  values is given by the Morse function

$$V(R) = D_e \{ 1 - \exp[-a(r - R_0)] \}^2$$

The Morse potential gives zero potential energy at the equilibrium bond length  $R_0$ . As the internuclear distance  $R$  approaches infinity,  $V(R)$  approaches the **bond dissociation energy**,  $D_e$ .

Solving Schrödinger's equation using the **Morse potential** (instead of the harmonic potential) gives the vibrational energy levels

$$E_n = v_e \left( n + \frac{1}{2} \right) - x_e v_e \left( n + \frac{1}{2} \right)^2$$

with

$$D_e = \frac{v_e}{4x_e}$$

$v_e$  is the fundamental vibration frequency, corrected for anharmonicity, and  $x_e$  is the **anharmonicity constant**.

Fitting the corrected energy equation

$$E_{nJ} = v_e \left( n + \frac{1}{2} \right) - x_e v_e \left( n + \frac{1}{2} \right)^2 + BJ(J + 1) - DJ^2(J + 1)^2$$

to measured high resolution rotational-vibrational spectra gives moments of inertia, centrifugal distortion constants, accurate fundamental vibration frequencies, bond dissociation energies, and anharmonicity constants.

## Spectroscopic Parameters for Ground-State Diatomic Molecules

Molecule	$\tilde{B}/\text{cm}^{-1}$	$\tilde{D}/\text{cm}^{-1}$	$\tilde{\nu}_e/\text{cm}^{-1}$	$x_e \tilde{\nu}_e/\text{cm}^{-1}$	$R_0/\text{pm}$	$D_e/\text{kJ mol}^{-1}$
H <sub>2</sub>	60.80	0.0463	4395.2	117.90	74.16	431.8
H <sup>35</sup> Cl	10.591	0.0005	2989.7	52.05	127.46	428.6
H <sup>79</sup> Br	8.473	0.0003	2649.7	45.21	141.3	361.8
<sup>12</sup> C <sup>16</sup> O	1.931	0.0001	2170.2	13.46	112.81	1071.6
<sup>14</sup> N <sup>16</sup> O	1.705	0.0001	1904.0	13.97	115.08	626.1
<sup>14</sup> N <sup>14</sup> N	2.010	0.0001	2359.6	14.46	109.4	941.2
<sup>16</sup> O <sup>16</sup> O	1.446	0.0001	1580.4	12.07	120.74	490.1
<sup>35</sup> C <sup>35</sup> Cl	0.244	0.0001	564.9	4.0	198.8	238.8
<sup>7</sup> Li <sup>7</sup> Li	0.673	0.0009	<b>35.14</b>	<b>2.59</b>	267.2	99.4
<sup>23</sup> Na <sup>23</sup> Na	0.155	0.0001	159.2	0.76	307.8	70.4
<sup>35</sup> Cl <sup>19</sup> O	0.516	0.0001	793.2	9.9	162.81	252.4
<sup>23</sup> NaH	4.901	0.0001	1172.2	19.72	188.73	202.0



## Raman Spectroscopy

For a molecule to be microwave or IR active, it must have a permanent dipole moment or a dipole moment that changes with the vibrations, respectively.

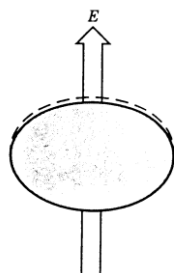
In addition to permanent dipoles, it is also possible to have **induced electric dipole moments** generated by electromagnetic radiation. If the electric cloud of a molecule is not spherically symmetric, for example, an oscillating electric field can produce small transient excesses and deficiencies in the electron density on opposite sides of the molecule, which appears as a small oscillating dipole moment.

The distortion of the electron density in an oscillating electric field is determined by its **polarizability**. In addition to a permanent dipole moment that a molecule might have, an applied electric field induces the transient (time-dependent) dipole moment

$$\vec{\mu}(t) = \alpha \vec{E}(t)$$

given by the polarizability tensor  $\alpha$ . Tensor element  $\alpha_{ik}$  gives the dipole moment along the  $i$ -axis generated by the component of the electric field along the  $k$ -axis.

$$\begin{pmatrix} \mu_x \\ \mu_y \\ \mu_z \end{pmatrix} = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{bmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix}$$



**Raman spectroscopy** deals with rotational and vibrational transitions caused by the interactions of radiation and induced dipole moments. Raman transitions, in general, are much weaker in intensity than transitions generated by permanent dipoles (*why?*). With high intensity laser radiation sources, however, this limitation can be overcome.

A molecule must have an **anisotropic polarizability** to be Raman active. In other words, its polarizability must not be the same in every direction.

### Selection Rules for Raman Rotational Spectra

All linear molecules, including all diatomics (homonuclear or heteronuclear), have anisotropic polarizabilities and are therefore Raman active. The electron density in H<sub>2</sub> molecules, for example, is more strongly distorted along the bond axis. This is important because **Raman spectra can be measured for infrared inactive molecules that lack a permanent dipole.**

Spherical rotors, such as SF<sub>6</sub> and CH<sub>4</sub>, have isotropic polarizabilities and therefore do not have rotational Raman spectra. They do not have permanent dipole moments, and are therefore microwave inactive. (Does this mean that spherical rotors are not rotating?)

#### Rotational Raman selection rules:

**Linear Rotors**                       $\Delta J = 0, \pm 2$

**Symmetric Rotors**               $\Delta J = 0, \pm 1, \pm 2$  and  $\Delta K = 0$

The  $\Delta J = 0$  transitions do not lead to changes in the energy or the frequency of scattered photons. They contribute to the unshifted Rayleigh radiation (important for light scattering measurements).

The  $\Delta J = \pm 2$  transitions can be understood in terms of conservation of momentum by noting that two spin-1 photons are involved (the incoming photon and the scattered photon), so the maximum change in the angular momentum quantum number is  $\pm 2$ .

## Raman Rotational Spectra for Linear Rotors

The selection rules  $\Delta J = 0, \pm 2$  can be used to predict the form of Raman spectra for linear rotors, such as diatomic molecules.

Rayleigh Line For incident radiation with frequency  $\nu_I$ , the Rayleigh line for radiation scattered with no change in energy appears at frequency  $\nu_I$ . ( $\Delta J = 0$ )

Stokes Lines When a molecule makes a transition with  $\Delta J = +2$ , the scattered radiation leaves the molecule with higher rotational energy, so there is a decrease in the frequency and the energy of the scattered radiation. The transitions with  $\Delta J = +2$  are called the **Stokes lines**.

For incident radiation at frequency  $\nu_0$ , the rotational energy equation  $E_J = BJ(J + 1)$  can be used to predict transitions at the frequencies  $\nu_I - (6B/h)$ ,  $\nu_I - (10B/h)$ ,  $\nu_I - (14B/h)$ ,  $\nu_I - (18B/h)$ , ... with spacing  $4B/h$ .

**$J \rightarrow J + 2$  (Stokes lines (molecules pick up energy)):**

$$0 \rightarrow 2 \quad \Delta E = B(2)(2+1) - B(0)(0+1) = 6B$$

$$1 \rightarrow 3 \quad \Delta E = B(3)(3+1) - B(1)(1+1) = 10B$$

$$2 \rightarrow 4 \quad \Delta E = B(4)(4+1) - B(2)(2+1) = 14B$$

$$3 \rightarrow 5 \quad \Delta E = B(5)(5+1) - B(3)(3+1) = 18B$$

*etc.*

Anti-Stokes Lines When a molecule makes a transition with  $\Delta J = -2$ , the scattered radiation leaves the molecule with lower rotational energy, so there is an increase in the frequency and the energy of the scattered radiation. Transitions with  $\Delta J = -2$  are called the **anti-Stokes lines**.

For incident radiation at frequency  $\nu_I$ , the energy equation  $E_J = BJ(J + 1)$  can be used to predict transitions at the frequencies  $\nu_I + (4B/h)$ ,  $\nu_I + (10/h)$ ,  $\nu_I + (14B/h)$ ,  $\nu_I + (18B/h)$ , ... with spacing  $4B/h$  once again.

**$J \rightarrow J - 2$  (Anti-Stokes lines (molecules lose energy)):**

$$2 \rightarrow 0 \quad \Delta E = B(0)(0+1) - B(2)(2+1) = -6B$$

$$3 \rightarrow 1 \quad \Delta E = B(1)(1+1) - B(3)(3+1) = -10B$$

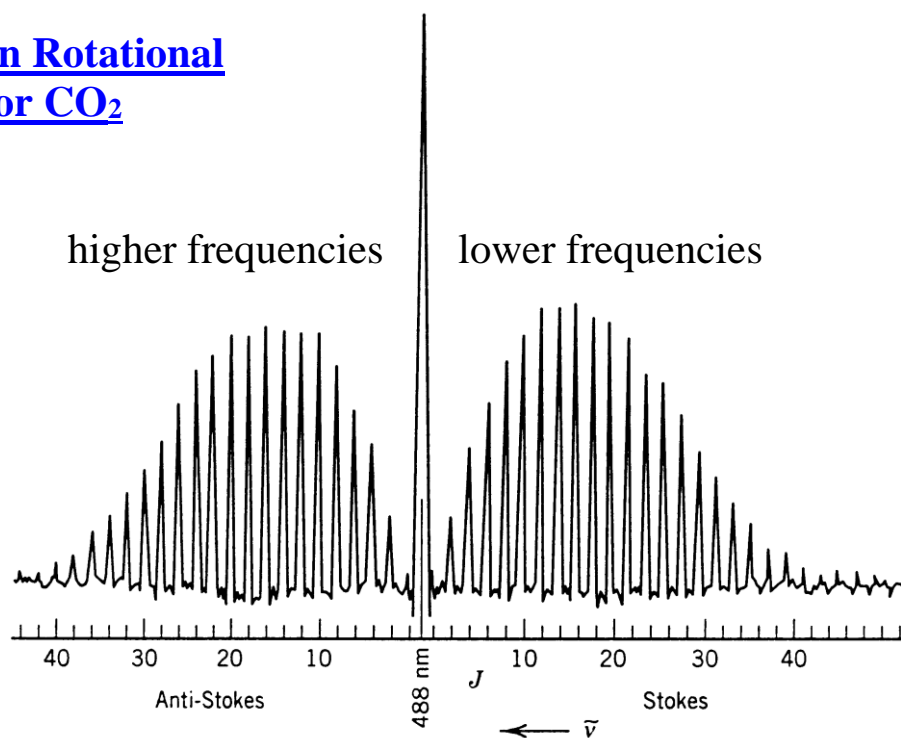
$$4 \rightarrow 2 \quad \Delta E = B(2)(2+1) - B(4)(4+1) = -14B$$

$$5 \rightarrow 3 \quad \Delta E = B(3)(3+1) - B(5)(5+1) = -18B$$

*etc.*

Rayleigh Line  
(unshifted)

**Pure Raman Rotational Spectrum for CO<sub>2</sub>**



## Raman Vibrational Spectra for Diatomics

The main selection rule for vibrational Raman transitions is that the polarizability of the molecule must change during vibration. The vibration of homonuclear and heteronuclear molecules causes the electron clouds to expand and contract, and so the polarizability changes. Both kinds of diatomics are therefore vibrationally Raman active. (In contrast, only heteronuclear diatomics are vibrationally infrared active.)

The selection rule for vibrational Raman transitions is  $\Delta n = \pm 1$ . The anti-Stokes lines are shifted to higher frequencies because the scattered photon picks up energy from an excited vibrational state and leaves the molecule in a lower-energy state ( $\Delta n = -1$ ).

The spacing of vibrational energy levels is large compared to thermal energies at room temperature. Consequently, most molecules are in their ground vibrational states under ambient conditions, and vibrational **anti-Stokes lines are relatively weak**.

The lower-frequency Stokes lines corresponding to  $\Delta n = +1$  (the scattered radiation leaves the molecules in a higher vibrational state) are more intense.

In gas-phase Raman spectroscopy, simultaneous vibrational and rotational transitions produce a band structure with multiple lines.

In the terminology used by spectroscopists, the O branch, Q branch, and S branch correspond to **Stokes lines ( $\Delta n = +1$ )** with the following branches:

**O branch**       $\Delta J = -2$

**Q branch**       $\Delta J = 0$

**S branch**       $\Delta J = +2$

**$n \rightarrow n + 1, J \rightarrow J + 2$  (S Branch):**

$$0 \rightarrow 2 \quad \Delta E = h\nu_0 + B(2)(2+1) - B(0)(0+1) = h\nu_0 + 6B$$

$$1 \rightarrow 3 \quad \Delta E = h\nu_0 + B(3)(3+1) - B(1)(1+1) = h\nu_0 + 10B$$

$$2 \rightarrow 4 \quad \Delta E = h\nu_0 + B(4)(4+1) - B(2)(2+1) = h\nu_0 + 14B$$

$$3 \rightarrow 5 \quad \Delta E = h\nu_0 + B(5)(5+1) - B(3)(3+1) = h\nu_0 + 18B$$

*etc.*

**$n \rightarrow n + 1, J \rightarrow J$  (Q Branch):**

$$J \rightarrow J \quad \Delta E = h\nu_0$$

**$n \rightarrow n + 1, J \rightarrow J - 2$  (O Branch):**

$$2 \rightarrow 0 \quad \Delta E = h\nu_0 + B(0)(0+1) - B(2)(2+1) = h\nu_0 - 6B$$

$$3 \rightarrow 1 \quad \Delta E = h\nu_0 + B(1)(1+1) - B(3)(3+1) = h\nu_0 - 10B$$

$$4 \rightarrow 2 \quad \Delta E = h\nu_0 + B(2)(2+1) - B(4)(4+1) = h\nu_0 - 14B$$

$$5 \rightarrow 3 \quad \Delta E = h\nu_0 + B(3)(3+1) - B(5)(5+1) = h\nu_0 - 18B$$

*etc.*

The information available from Raman spectroscopy adds to that from infrared spectroscopy because homonuclear diatomics can be studied, providing force constants, bond lengths, fundamental frequencies, and other information.

## Vibrational-Rotational Raman Spectrum for a Diatomic Molecule

