

Molecular Spectroscopy and Photochemistry

What is Spectroscopy?

- The study of molecular structure and dynamics through the absorption, emission and scattering of light.

or

- Spectroscopy is the study of the interactions of matter with electromagnetic radiation and the extraction of information about molecular structure from this study

Emission/Absorption Spectroscopy and Energy Levels

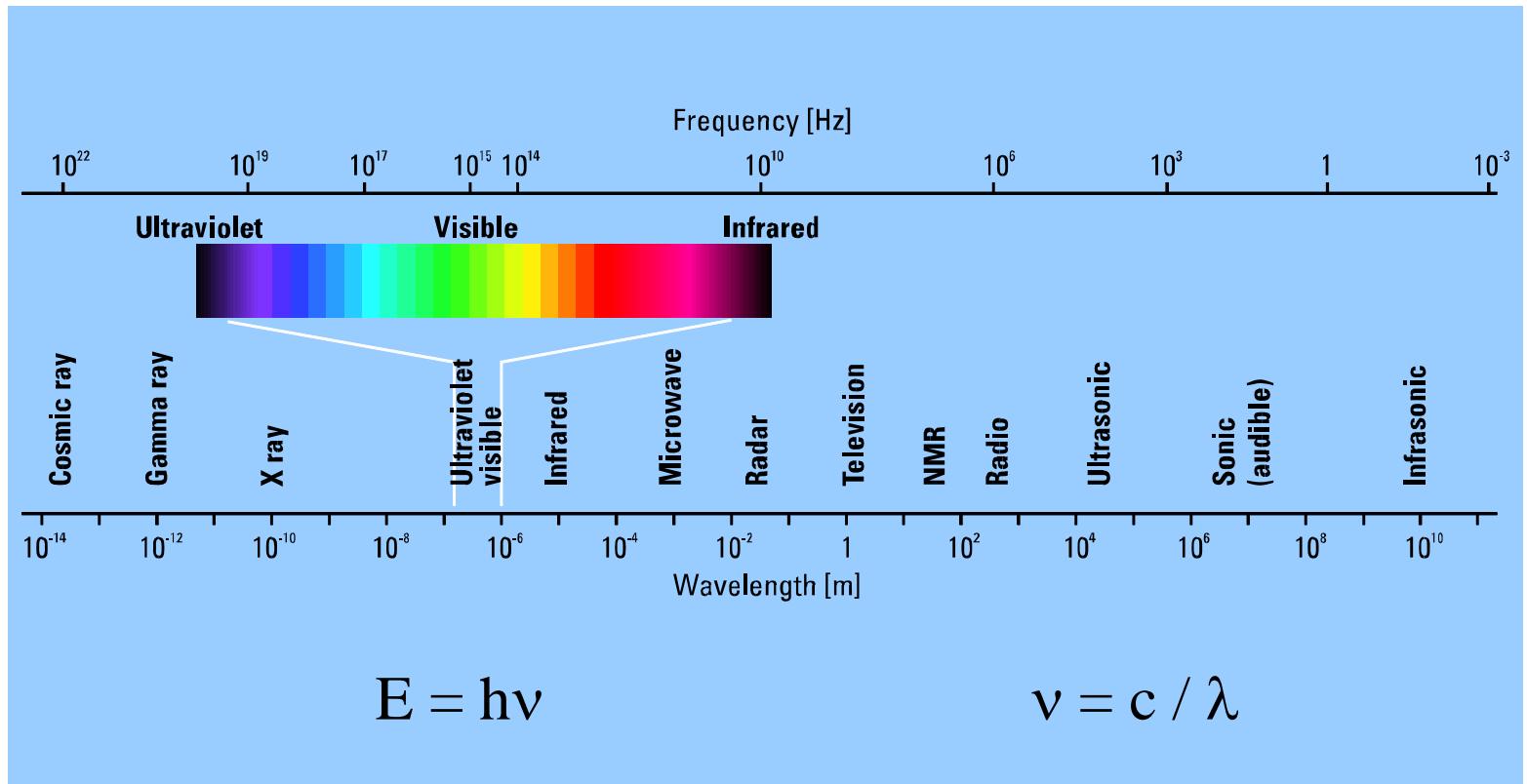
- The energy levels of atoms and molecules can be studied experimentally by measuring the wavelengths of the light that is emitted, absorbed, or scattered in transitions between energy levels.
- $E_{Photon} = h\nu = \frac{hc}{\lambda}$

- This is an expression of the conservation of energy and is expressed by the *Bohr frequency rule*:

$$E_{\text{photon}} = h\nu = E_{\text{upper}} - E_{\text{lower}}$$

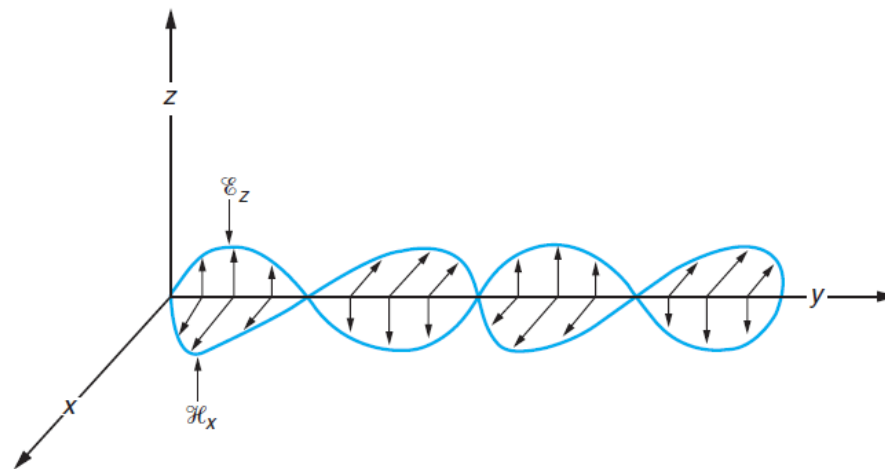
- The Bohr frequency rule is based on the assumption that only one photon is absorbed or emitted at a time.
- Multiphoton transitions can also occur.

The Electromagnetic Spectrum



Regions of the Electromagnetic Spectrum

Name of Region	Wavelength	Photon Energy/eV
Gamma radiation	< 10 pm	> 124000
X-radiation	10 pm–10 nm	124000–124
Ultraviolet radiation	10 nm–400 nm	124–3.1
Visible radiation(light)	400 nm–750 nm	3.1–1.65
Infrared radiation	750 nm–1 mm	1.65–0.00124
Microwave radiation (including radar)	1 mm–10 cm	0.00124–0.00124
Radio-frequency radiation (including AM, FM, TV)	10 cm–10 km	< 0.00124



- Spacings between electronic energy levels correspond to photon energies in the visible and ultraviolet regions.
- Spacings between vibrational energy levels correspond to photon energies in the infrared region.
- Spacings between rotational energy levels correspond to photon energies in the microwave region.
- Spacings between translational energy levels are too small to observe spectroscopically.

- *Photochemistry* involves absorption of photons that can break chemical bonds or
- cause transitions to reactive excited states.
- Typical chemical bond energies are roughly 400 to 1000 kJ mol⁻¹.
- Photons with energies large enough to break chemical bonds lie in the ultraviolet region.

EXAMPLE 23.1

Find the frequency and wavelength of a photon with enough energy to break a chemical bond with bond energy of 4.31 eV (corresponding to 416 kJ mol⁻¹), which is the average bond energy of a C-H bond.

Solution

$$\nu = \frac{E}{h} = \frac{(4.31 \text{ eV})(1.602 \times 10^{-19} \text{ J (eV)}^{-1})}{6.6261 \times 10^{-34} \text{ J s}} = 1.04 \times 10^{15} \text{ s}^{-1}$$

$$\lambda = \frac{2.9979 \times 10^8 \text{ m s}^{-1}}{1.04 \times 10^{15} \text{ s}^{-1}} = 2.88 \times 10^{-7} \text{ m} = 288 \text{ nm}$$

The Quantum Mechanics of Spectroscopic Transitions

- Stationary states of atomic and molecular systems can be described by the time-independent Schrodinger equation.
- Spectroscopy involves a time-dependent process, the evolution of the state of a system containing atoms or molecules plus electromagnetic radiation.

- Electromagnetic radiation consists of an oscillating electric field and an oscillating magnetic field
- A transition produced by the electric field is called an *electric dipole transition*, and a transition due to the magnetic field is called a *magnetic dipole transition*.
- The electric dipole transitions dominate in optical spectroscopy.
- Magnetic dipole transitions are involved in nuclear magnetic resonance (NMR) spectroscopy and electron spin resonance (ESR) spectroscopy

- *Time-dependent perturbation theory* is applied to study electric dipole transitions.

$$\hat{H} = \hat{H}^{(0)} + \hat{H}'$$

- $\hat{H}^{(0)}$ is the complete time-independent Hamiltonian operator of the molecule in the absence of radiation.
- The perturbation term \hat{H}' describes the interaction between the molecule and the electric field of the radiation, and is time-dependent because of the oscillation of the radiation.

- We assume that the zero-order time-independent Schrodinger equation has been solved to a usable approximation:

$$\hat{H}^{(0)}\psi_j^{(0)} = E_j^{(0)}\psi_j^{(0)}$$

- The wave function $\psi_j^{(0)}$ is one of the energy eigenfunction of the molecule in the absence of radiation.
- Inclusion of the perturbation produces a time-dependent wave function, which is written as a linear combination of the zero-order wave functions:
- $\Psi(q, t) = \sum_j a_j(t)\psi_j^{(0)}(q)$

- In order to observe transitions we specify that at time $t = 0$ the wave function is equal to one of the zero-order functions, $\psi_n^{(0)}$,

$$\Psi(q, t) = \psi_n^{(0)}(q)$$

- so that at $t = 0$ only a_n is nonzero:

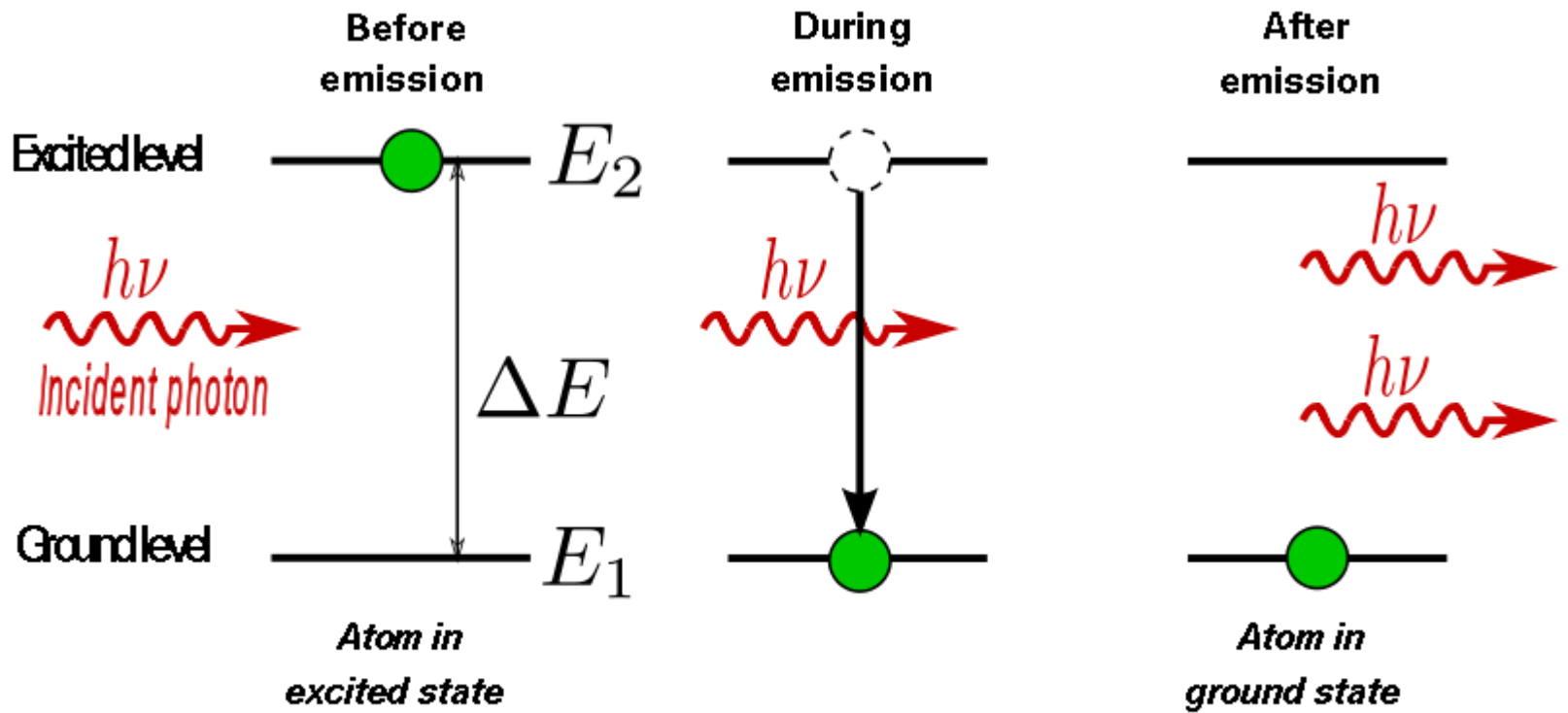
$$a_n = \delta_{jn} = \begin{cases} 1 & \text{if } j = n \\ 0 & \text{if } j \neq n \end{cases}$$

- where δ_{jn} is the *Kronecker delta*. If δ_{jn} times another coefficient, a_j , becomes nonzero, this corresponds to a nonzero probability of a transition from the state $\psi_n^{(0)}$ to the state $\psi_j^{(0)}$.

- Time-dependent perturbation theory provides an approximate formula that gives the coefficients as functions of time.
- If the radiation is polarized with its electric field in the z direction, $|a_j(t)|^2$ is proportional to the intensity of the radiation of the wavelength that satisfies the Bohr frequency rule and is also proportional to the square of the following integral:
 - $(\mu_z)_{jn} = \int \psi_j^{(0)*} \hat{\mu}_z \psi_n^{(0)} dq$
 - This integral is the z component of the *transition dipole moment* for states n and j .

- For two states that have a nonzero transition dipole moment, a transition between them is predicted to occur “*allowed transition*”.
- A transition between two states that have a zero transition dipole moment is predicted not to occur, “*forbidden transition*”.
- A rule that tells which transitions are allowed is called a *selection rule*.
- Forbidden transitions frequently do occur, but generally with lower probabilities than allowed transitions.

- A transition that raises the energy of the atom or molecule corresponds to *absorption* of radiation, whereas one that lowers the energy corresponds to *stimulated emission* of radiation.
- Absorption is observed if the lower-energy state has a greater population than the higher-energy state, and stimulated emission is observed if the higher-energy state has a greater population.
- Stimulated emission has the same wavelength as the incident radiation, moves in the same direction, and is in phase with the incident radiation “**Coherent**”.

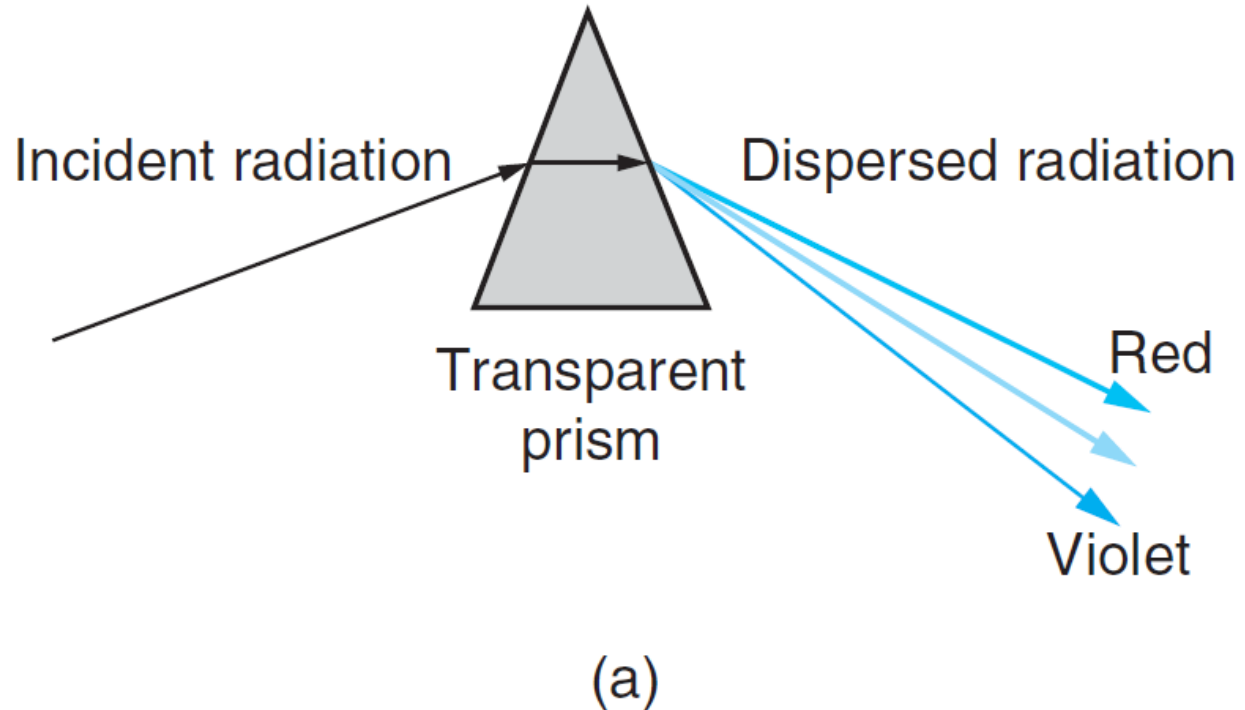


$$E_2 - E_1 = \Delta E = h\nu$$

- This kind of radiation is emitted by lasers, which amplify electromagnetic radiation by adding radiation to an incident beam by stimulated emission. “*Laser*” is an acronym for “*light amplification by stimulated emission of radiation.*”
- Transitions resulting in the emission of photons can also occur in the absence of stimulating radiation. This is called *spontaneous emission*.
- In *emission spectroscopy* spontaneously emitted radiation from excited atoms or molecules is observed.

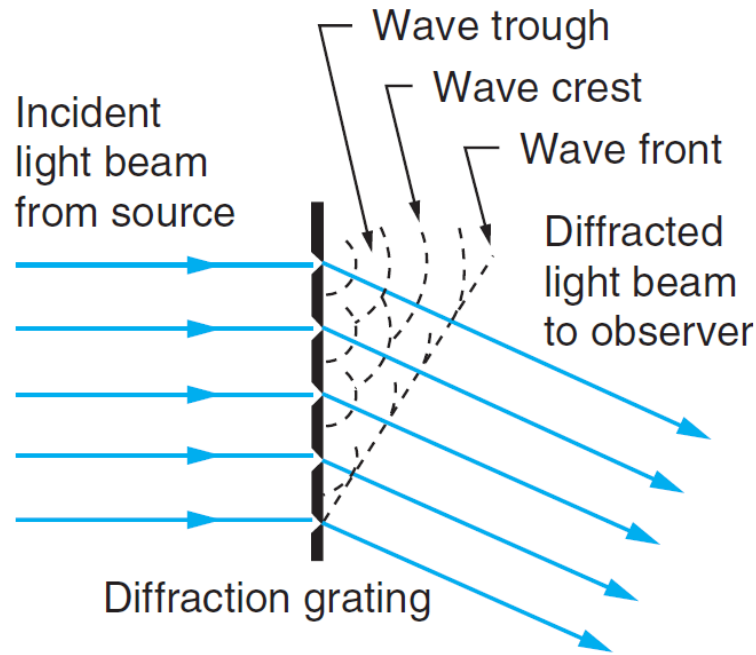
- In *absorption spectroscopy* the attenuation of an incident beam is observed.
- The amount of absorption of radiation depends on three things:
 - A. The intensity of the radiation.
 - B. the probability of transition.
 - C. The numbers of molecules in the initial state and in the final state.
- (Number of molecules in a state with energy E)
 $\propto e^{-E/k_B T}$

- The classical way to observe emission or absorption spectra is to *disperse* the radiation, which means separating the different wavelengths from each other.



The Dispersion of Electromagnetic Radiation.

(a) Prism: Since the refractive index depends on wavelength, different wavelengths are refracted through different angles.

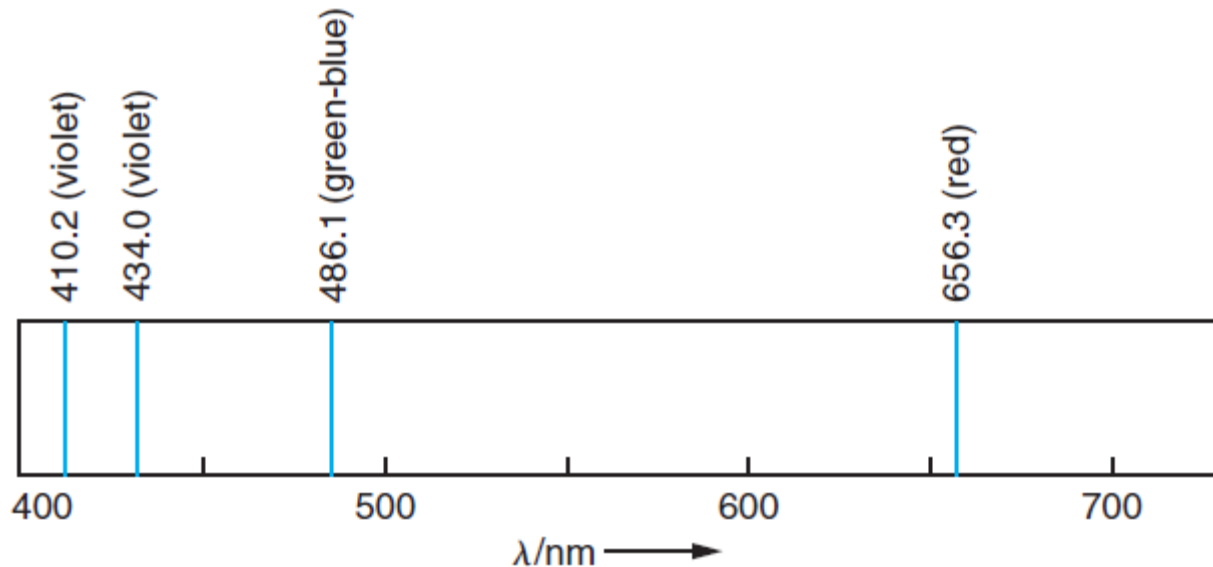


(b)

The Dispersion of Electromagnetic Radiation.

(b) Transmission grating: Since constructive interference is necessary to give the diffracted beam, different wavelengths are diffracted through different angles.

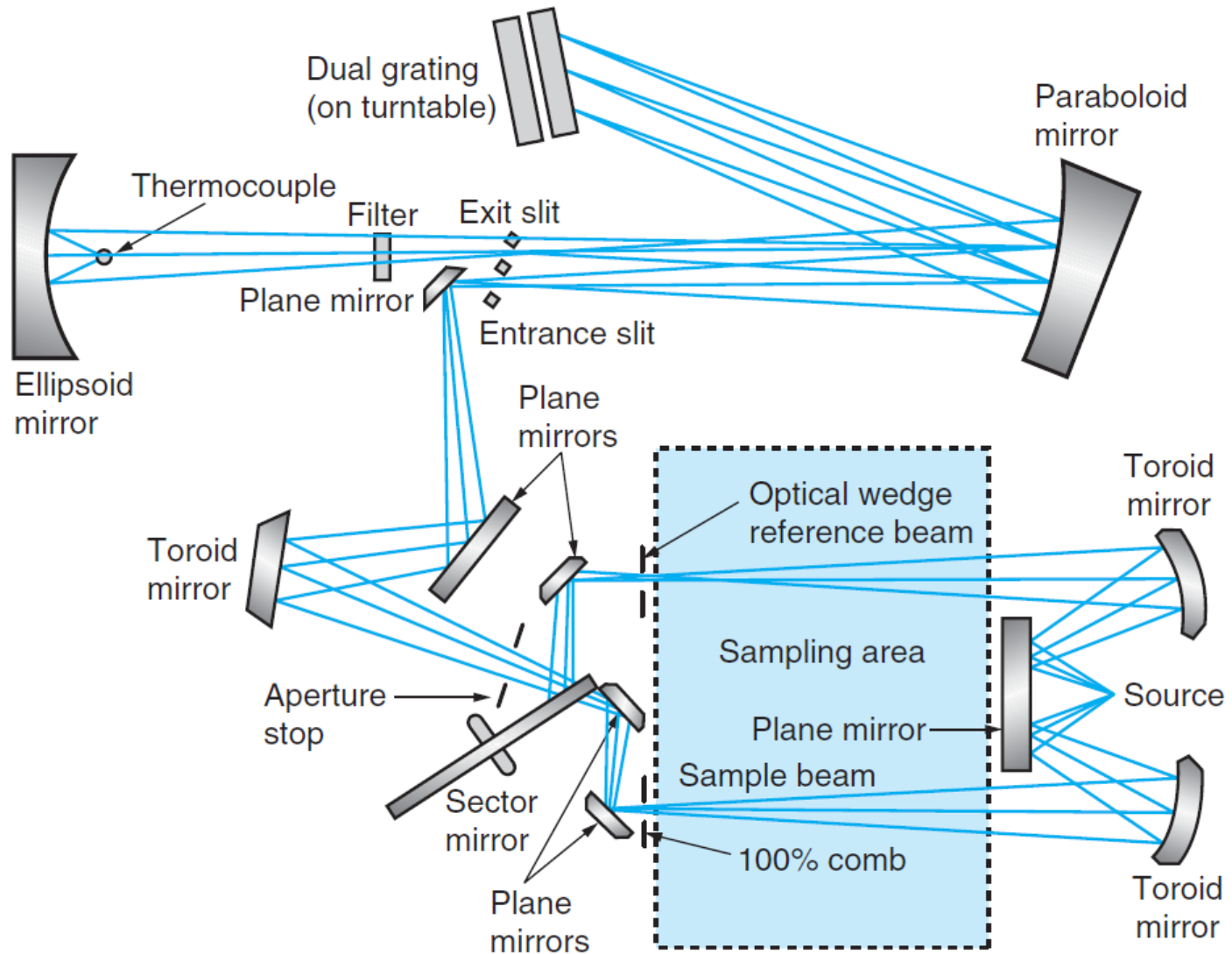
- In a simple spectroscope, the wavelengths of emitted light are observed by viewing the dispersed radiation
- If only narrow bands of wavelengths are emitted, the slit images look like line segments and are called *spectral lines*.



The Visible Portion of the Hydrogen Atom Emission Spectrum (Simulated).

Absorption Spectroscopy

- Absorption spectroscopy has traditionally been carried out in a *spectrophotometer*



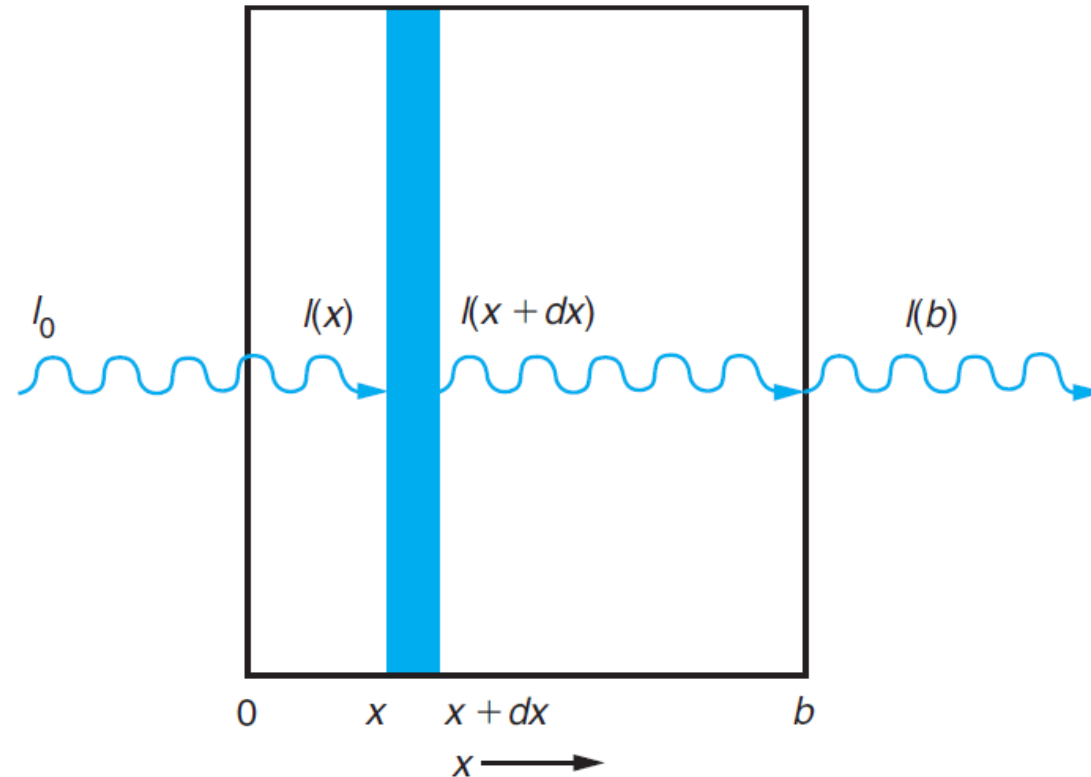
- The wavelength can be chosen by turning the prism or grating, and this is done automatically in a scanning instrument.
- A photocell or other detector determines the intensity of transmitted radiation.
- In a single-beam instrument, the cell containing the sample substance and a “blank” cell not containing this substance are placed alternately in the beam.
- In a double-beam instrument, the beam is divided and passed simultaneously through the sample cell and the blank cell.
- In a diode-array instrument, a number of detectors in different locations are used, and the entire spectrum is taken at one time.

- The intensity of a collimated beam of radiation is defined as the energy passing unit area per unit time.
- We define a total intensity, I_{tot} , which is the energy of all wavelengths per unit area per unit time, and an intensity per unit wavelength interval, $I(\lambda)$.
- The energy carried by radiation with wavelengths in the infinitesimal wavelength range between λ and $\lambda + d\lambda$ is
(Energy in range $d\lambda$ per unit time per unit area) = $I(\lambda)d\lambda$
- variable that is commonly plotted to represent an absorption spectrum is the *transmittance*, $T(\lambda)$, usually expressed in percent:

$$\bullet \quad T(\lambda) = \left(\frac{I(\lambda)_{\text{out}}}{I(\lambda)_{\text{in}}} \right) \times 100\% \quad (\text{definition of transmittance})$$

where $I(\lambda)_{\text{out}}$ is the intensity after the light beam passes through the cell and $I(\lambda)_{\text{in}}$ is the incident intensity.

The Beer–Lambert Law



- **Absorption of Light in a Thin Slab.** The attenuation of the light due to the absorbing substance in the thin slab is assumed to be proportional to the concentration of the substance and to the thickness of the slab.

$$\begin{aligned}
 -dI &= k(\lambda)Icdx \\
 -\frac{dI}{I} &= k(\lambda)cdx \\
 -\int_{I(0)}^{I(b)} \frac{dI}{I} &= k(\lambda)c \int_0^b dx \\
 -\ln\left(\frac{I(\lambda, b)}{I(\lambda, 0)}\right) &= \ln\left(\frac{I(\lambda, 0)}{I(\lambda, b)}\right) = k(\lambda)cb
 \end{aligned}$$

The *absorbance* $A(\lambda)$ (formerly called the *optical density*) is defined as the common logarithm of the same ratio as in the second natural logarithm

$$A(\lambda) = \log_{10}\left(\frac{I(\lambda, 0)}{I(\lambda, b)}\right) = \log_{10}\left(\frac{100\%}{T}\right)$$

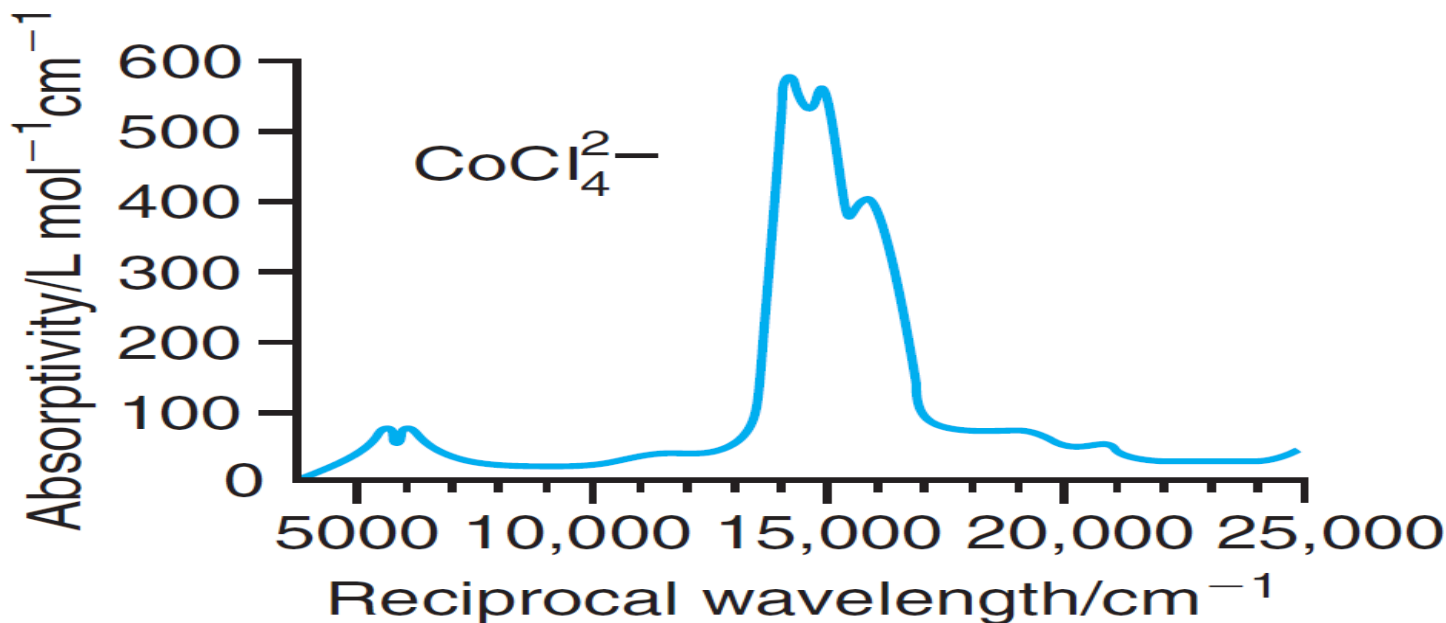
The Beer–Lambert law is:

$$A(\lambda) = a(\lambda)bc$$

where $a(\lambda)$ is the absorptivity (formerly called the extinction coefficient):

$$a(\lambda) = \frac{k(\lambda)}{\ln(10)} = \frac{k(\lambda)}{2.302585}$$

The absorptivity depends on λ , the absorbing substance and the solvent. If the concentration is measured in mol L⁻¹, the absorptivity is called the *molar absorptivity*.



EXAMPLE 23.2

A solution of a certain dye has a molar absorptivity of $1.8 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ at a wavelength of 606 nm. Find the concentration of a solution of this dye that has an absorbance at this wavelength equal to 1.65 in a cell 1.000 cm in length.

Solution

$$c = \frac{A}{ab} = \frac{1.65}{(1.8 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1})(1.000 \text{ cm})} = 9.2 \times 10^{-6} \text{ mol L}^{-1}$$

The Spectra of Atoms

The Hydrogen Atom

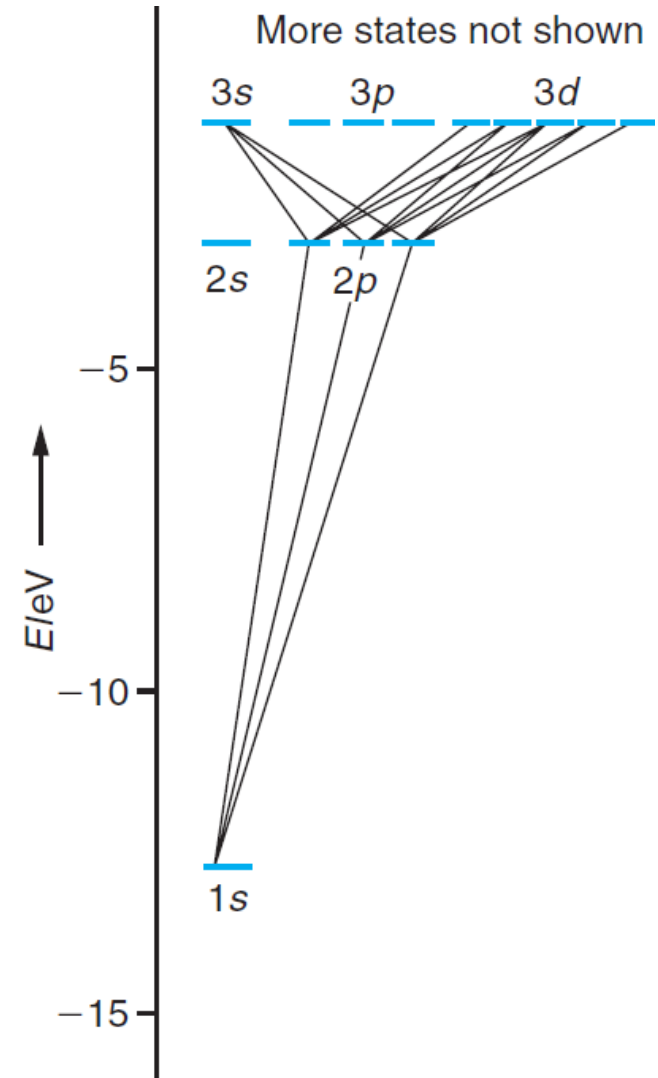
Hydrogen Atom Selection Rules

$$\Delta m = m_{\text{final}} - m_{\text{initial}} = 0, \pm 1$$

$$\Delta l = l_{\text{final}} - l_{\text{initial}} = \pm 1$$

Δn : no restrictions

The Energy Levels of the Hydrogen Atom and the Allowed Transitions between Them.



EXAMPLE 23.3

From Rydberg's formula in Eq. (14.4-10), find the wavelength and frequency of the photons emitted by a hydrogen atom undergoing the $n = 2 \rightarrow n = 1$ transition.

Solution

$$\frac{1}{\lambda} = R \left(\frac{1}{n_1} - \frac{1}{n_2} \right) = (109678 \text{ cm})^{-1} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

For the $n = 2$ to $n = 1$ transition

$$\frac{1}{\lambda} = (109678 \text{ cm}^{-1}) \left(\frac{1}{1} - \frac{1}{4} \right) = 82258 \text{ cm}^{-1}$$

$$\lambda = \frac{1}{82258 \text{ cm}^{-1}} = 1.2157 \times 10^{-5} \text{ cm} = 121.568 \text{ nm, in the ultraviolet}$$

Rotational and Vibrational Spectra of Diatomic Molecules

Rotational Spectra of Diatomic Molecules

The transition dipole moment integral for a rotational transition is

$$(\mu)_{J_{M''}, J'_{M'}} = \int Y_{J'' M''}^* \mu Y_{J' M'} \sin(\theta) d\theta d\phi$$

The Y functions are the rotational wave functions (spherical harmonic functions) and $\mu = \mu(r, \vartheta, \varphi)$ is the dipole moment operator of the molecule in the Born–Oppenheimer approximation.

The selection rules that result are:

$\Delta J = \pm 1$ for a molecule with nonzero permanent dipole moment

All ΔJ values forbidden for a molecule with zero permanent dipole moment

The rotational selection rules are well obeyed by diatomic molecules with $^1\Sigma$ electronic states.

- In order for a molecule to interact with the electric field of the radiation, it must exhibit a periodically varying electric dipole moment of the correct frequency.
- A rotating diatomic molecule with a permanent dipole moment does present a periodically varying dipole to the radiation.
- If a molecule has no permanent dipole moment it does not exhibit any periodic variation in the dipole moment.
- Rotational transitions correspond to photon wavelengths in the microwave region.

From the selection rule, the photon energy for an allowed transition is

$$E_{\text{photon}} = h\nu = \frac{hc}{\lambda} = E_{\nu, J+1} - E_{\nu J}$$

where J is the value of the rotational quantum number for the lower-energy state and the vibrational quantum number ν has the same value for both states.

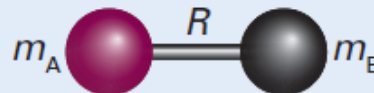
$$\tilde{\nu} = \frac{1}{\lambda} = \frac{1}{hc}(E_{\nu, J+1} - E_{\nu J})$$

$$\begin{aligned}\tilde{\nu} &= \frac{1}{\lambda} = \tilde{B}_e[(J+1)(J+2) - J(J+1)] \\ &= \tilde{B}_e[J^2 + 3J + 2 - J^2 - J] = 2\tilde{B}(J+1)\end{aligned}$$

Since J can take on values $0, 1, 2, \dots$, this corresponds to $2\tilde{B}, 4\tilde{B}$, and so on.

$$hc\tilde{B} = \frac{\hbar^2}{2I} \quad \text{so} \quad \tilde{B} = \frac{\hbar}{4\pi cI}$$

1. Diatomic molecules

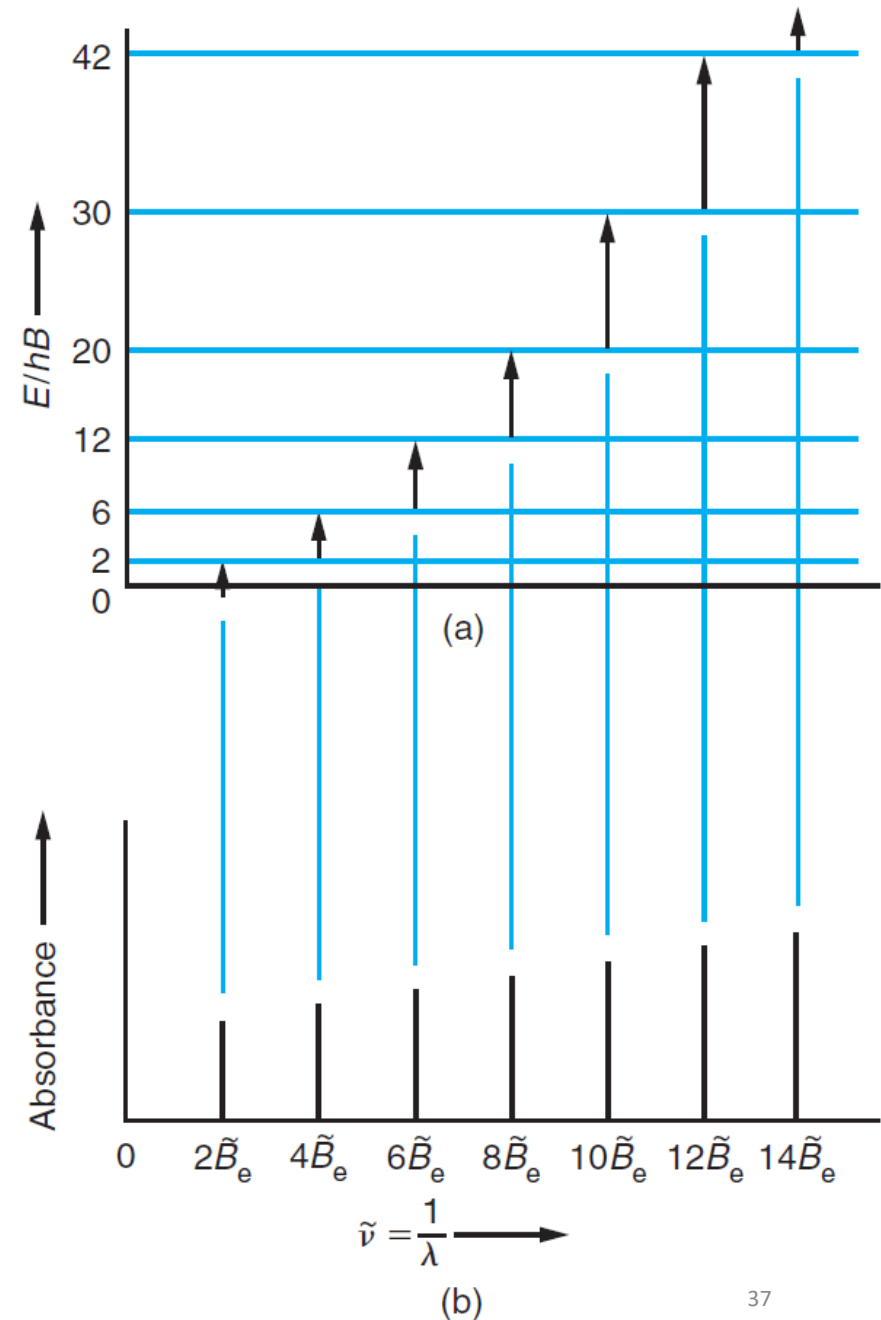


$$I = \mu R^2 \quad \mu = \frac{m_A m_B}{m}$$

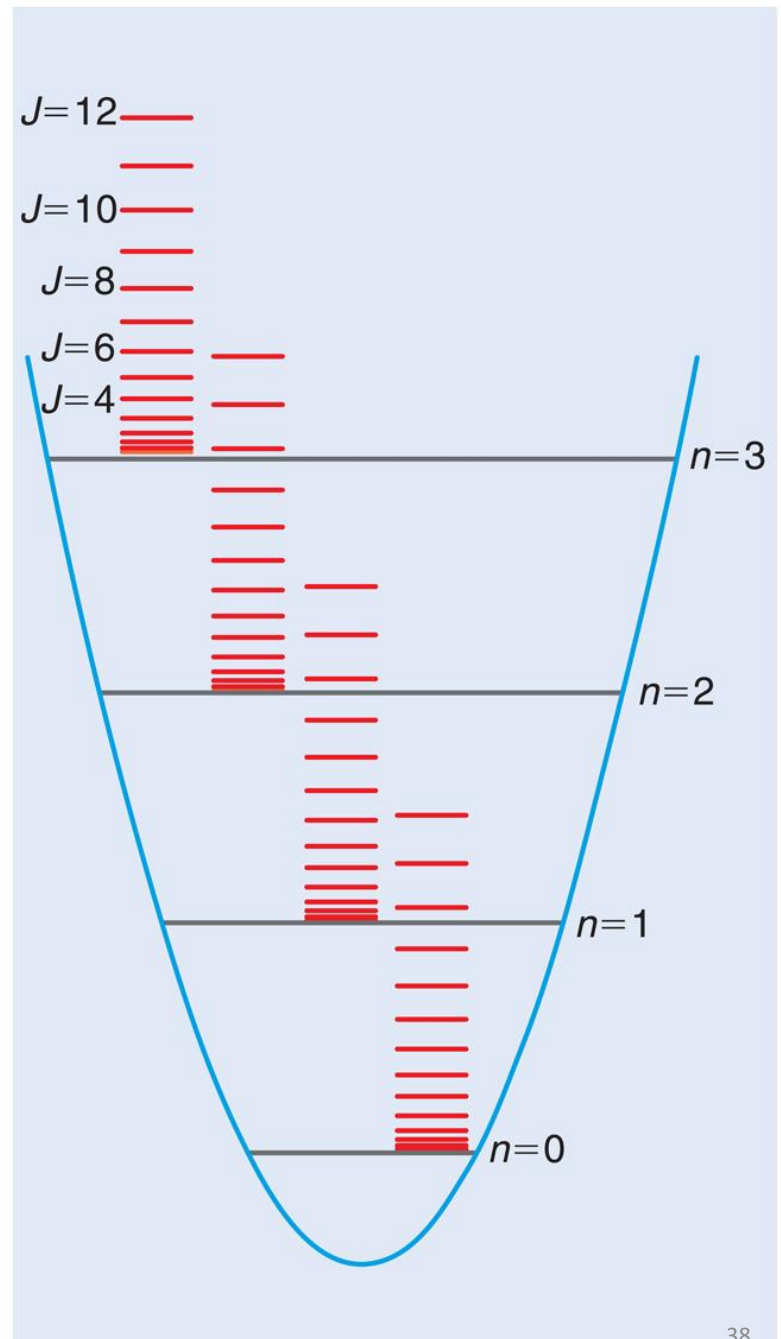
A Microwave Spectrum.

- (a) The allowed transitions.
- (b) The simulated spectrum.

The positions of the spectral lines are correlated with the transitions that produce the lines.



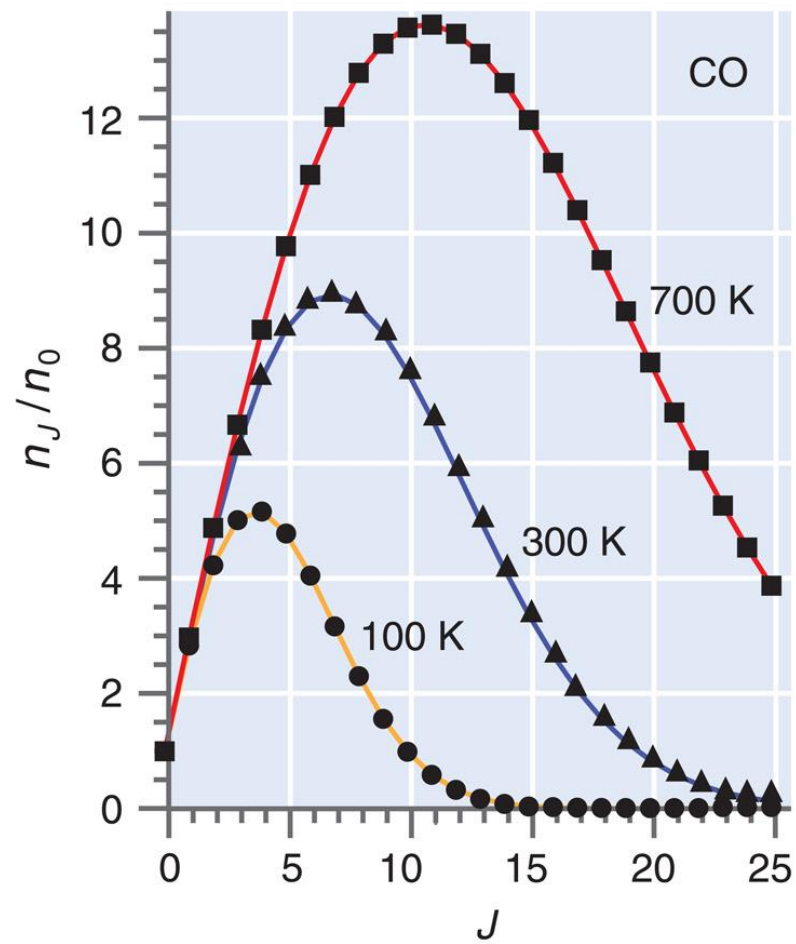
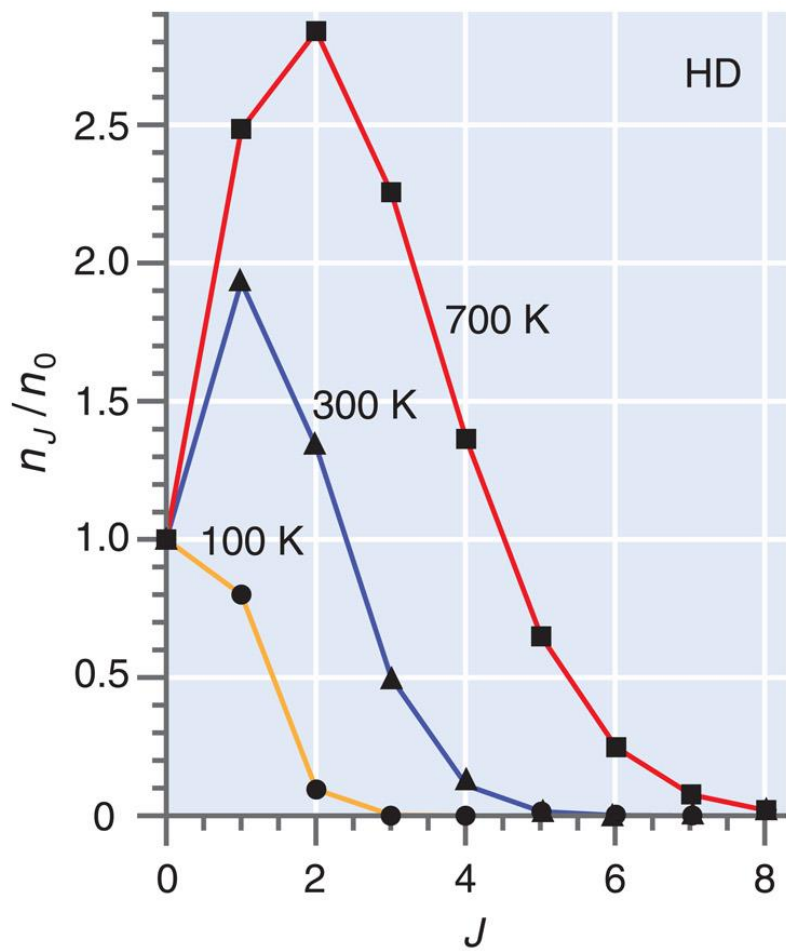
Schematic representation of rotational and vibrational levels.



The intensity of a given line in a spectrum is determined by the magnitude of the transition dipole moment for the transition that produces the spectral line and by the number of molecules occupying the initial state and the final state. At thermal equilibrium the population of a level is given by the Boltzmann distribution

$$\begin{aligned}(\text{Population of energy level } J) &\propto g_j e^{-E_J/k_B T} \\ &\propto (2J + 1) e^{-h B_e J(J+1)/k_B T}\end{aligned}$$

The degeneracy increases and the Boltzmann factor $e^{-E_J/k_B T}$ decreases as J increases, so the population rises to a maximum and then decreases as J increases.



Vibration–Rotation Spectra of Diatomic Molecules

When transitions are observed between vibrational energy levels, infrared radiation is emitted or absorbed. The vibrational selection rules are derived in the Born–Oppenheimer approximation by evaluating the transition dipole moment integral

$$(\mu_x)_{v'v''} = \int \psi_{v'}^* \hat{\mu}(x) \psi_{v''} dx$$

Using harmonic oscillator wave functions, the selection rule is

$$\Delta v = 0, \pm 1 \text{ for nonzero dipole moment}$$

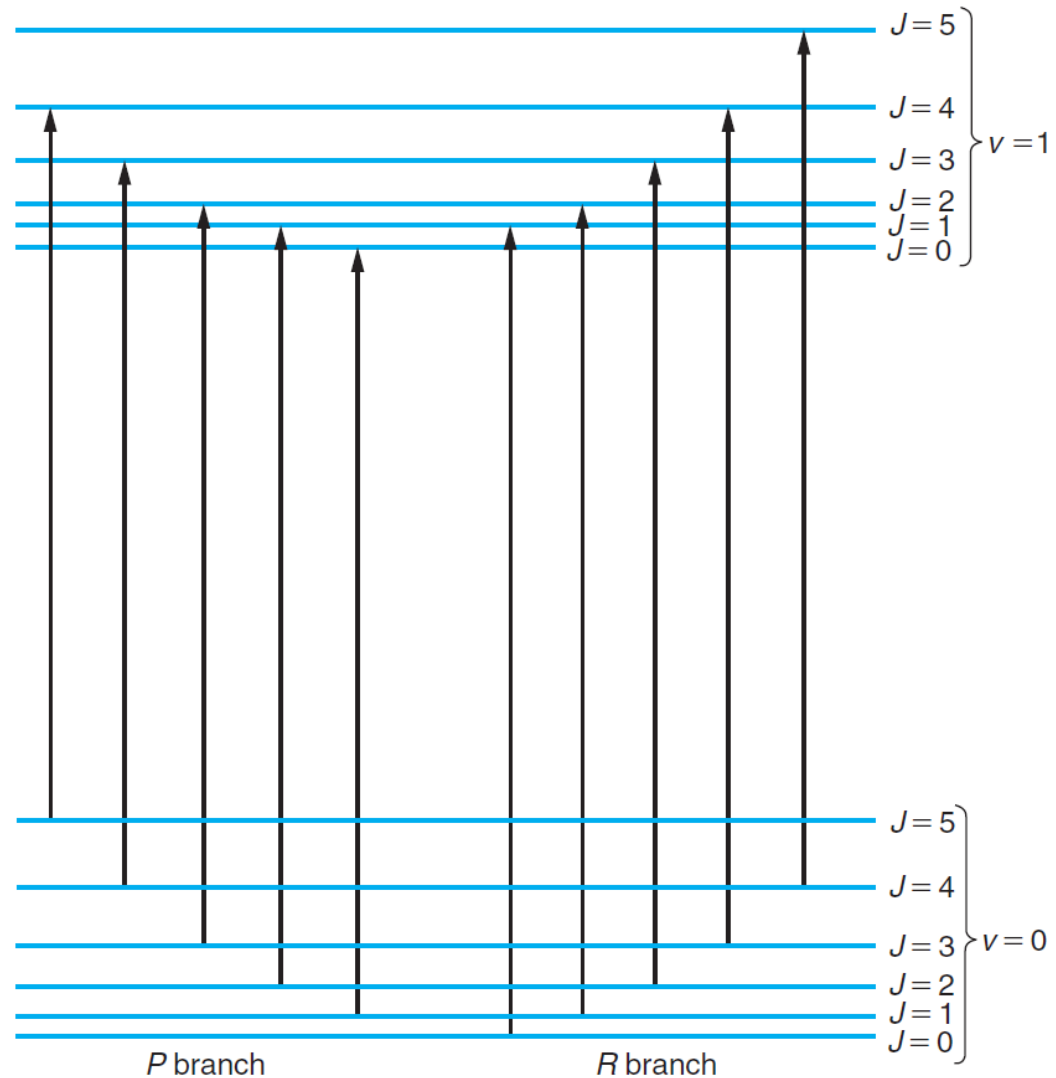
All Δv forbidden for zero dipole moment

- Since $\Delta v = 0$ is allowed giving the pure rotational spectrum in the microwave region.
- Transitions for which $\Delta v = \pm 1$ give spectra in the infrared region in which both rotational and vibrational quantum numbers change.
- Vibrational transitions do not occur without rotational transitions, because $\Delta J = 0$ is forbidden for diatomic molecules

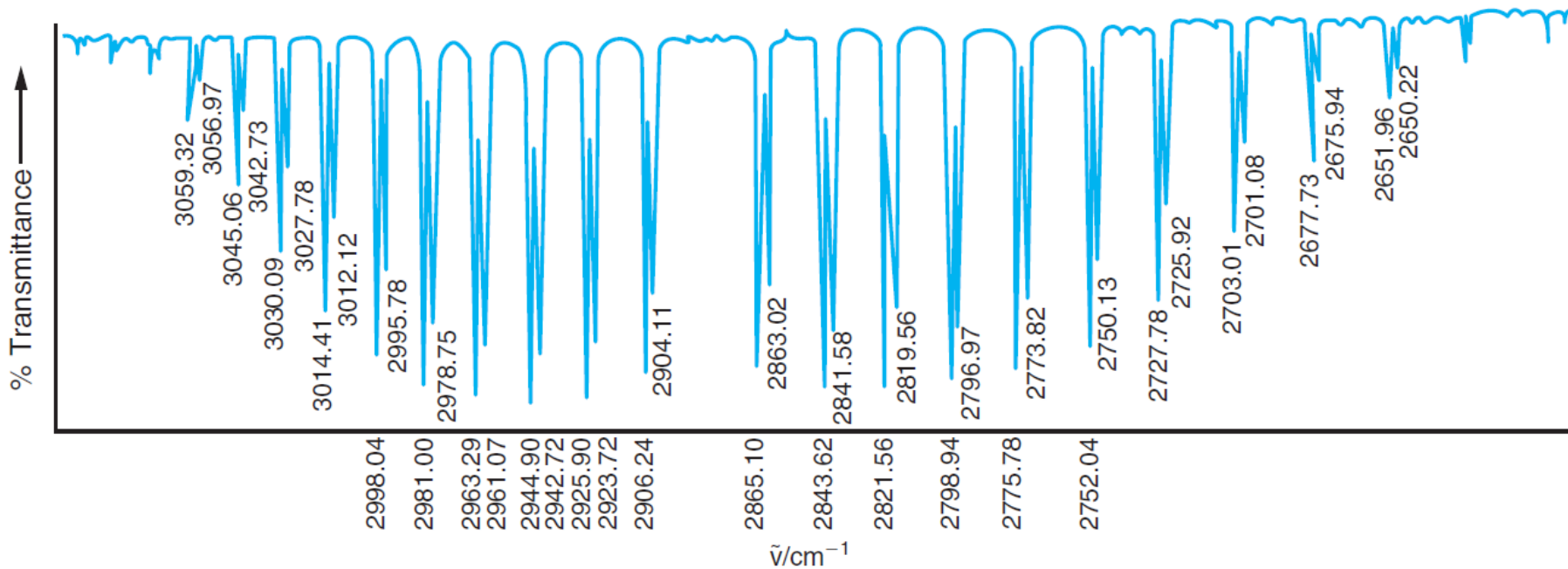
Allowed Transitions Leading to a Vibration– Rotation Spectral Band of a Diatomic Substance.

(fundamental band)

In the *R* branch, the value of *J* in the upper level is greater than that in the lower level, and in the *P* branch, the opposite is the case.



- The vibrational selection rules are less well obeyed than are the rotational selection rules, and forbidden vibrational transitions are frequently observed.
- A spectral band corresponding to $\Delta v = \pm 2$ is called *a first overtone*, one corresponding to $\Delta v = \pm 3$ is called *a second overtone*, and so on.
- Bands for which the lower value of v is larger than zero are called *hot bands*.
- Hot bands are generally not seen in absorption spectra near room temperature because of the small population of excited vibrational states.



The Fundamental Band of the Vibration–Rotation Spectrum of HCl. The resolution of the spectrum is sufficient to show the lines for H^{35}Cl and H^{37}Cl . The ^{35}Cl is the more abundant isotope of chlorine, and produces the more intense lines.

Electronic Spectra of Diatomic Molecules

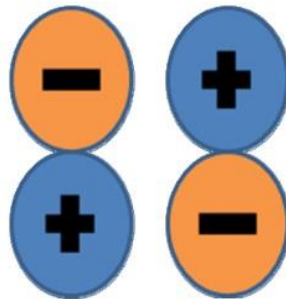
- The electronic spectra for most diatomic molecules are found in the ultraviolet and visible regions.
- The electronic transitions are usually accompanied by rotational and vibrational transitions.
- The following selection rules are obtained for electronic transitions in diatomic molecules:

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

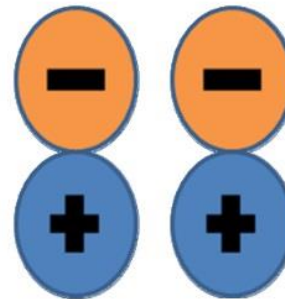
$$\Delta S = 0$$

Parity of electronic state changes: ($u \rightarrow g$ or $g \rightarrow u$)

- Where Λ is the quantum number of the total electronic orbital angular momentum and S is the total electron spin quantum number.



This pi orbital is gerade



This pi orbital is ungerade

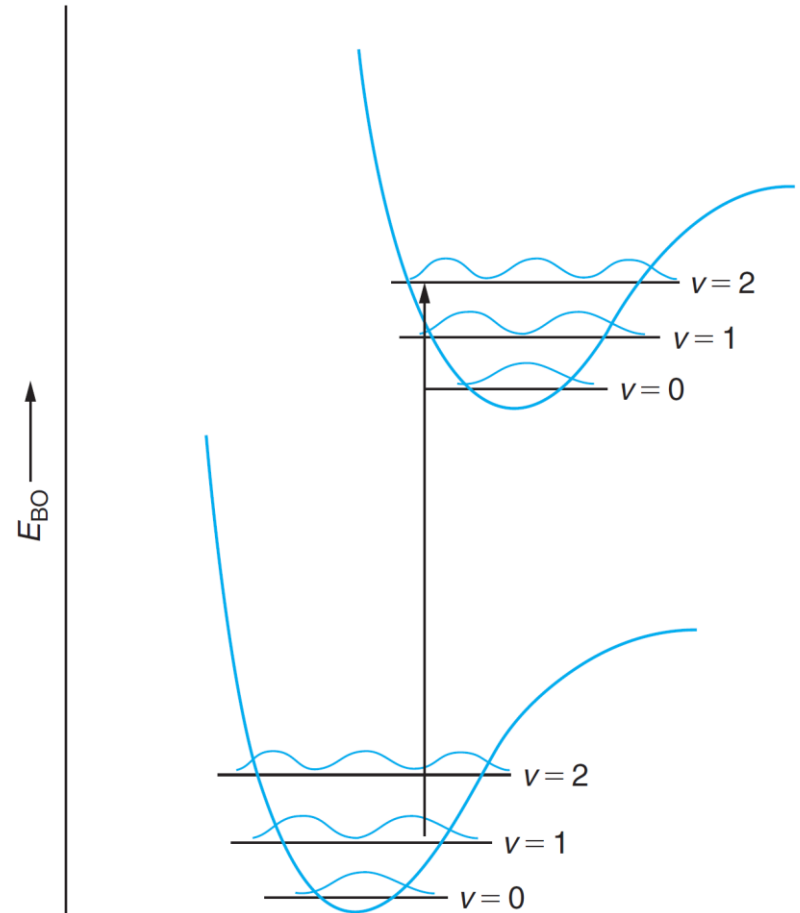
- The selection rules for the rotational and vibrational transitions that accompany electronic transitions are:
 - $\Delta J = \pm 1$
 - Δv : *not restricted*
- Forbidden transitions between triplet ($S = 1$) states and singlet ($S = 0$) states do occur, but with low probabilities compared with allowed transitions.
- Each electronic transition produces a number of bands, with one band for each vibrational transition and with the lines of each band corresponding to different rotational transitions.

- Measurement of electronic spectrum can yield the energy differences between electronic levels and between vibrational and rotational levels.

✱ The two curves are the Born–Oppenheimer electronic energies of two different electronic states.

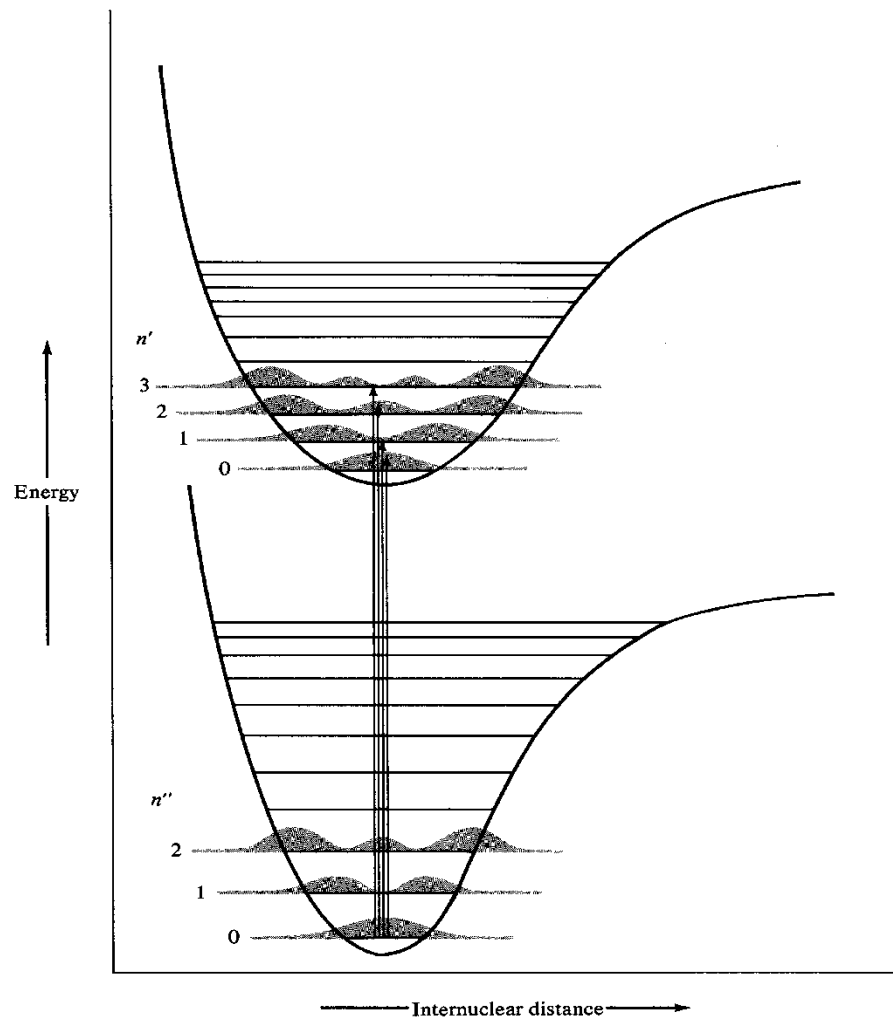
An Electronic Transition According to the Franck–Condon Principle.

A transition from the $v = 1$ state of the lower electronic state most likely will lead to the $v = 2$ state of the upper electronic state.



- *Franck–Condon principle* states that the nuclei do not move appreciably during an electronic transition. *This principle is closely related to the Born–Oppenheimer approximation.*
- One factor in the integrand of the transition dipole moment is the product of the vibrational wave functions in the initial and final states.
- Integration over the vibrational coordinate gives an overlap integral for the two vibrational states that is called the *Franck–Condon factor*.

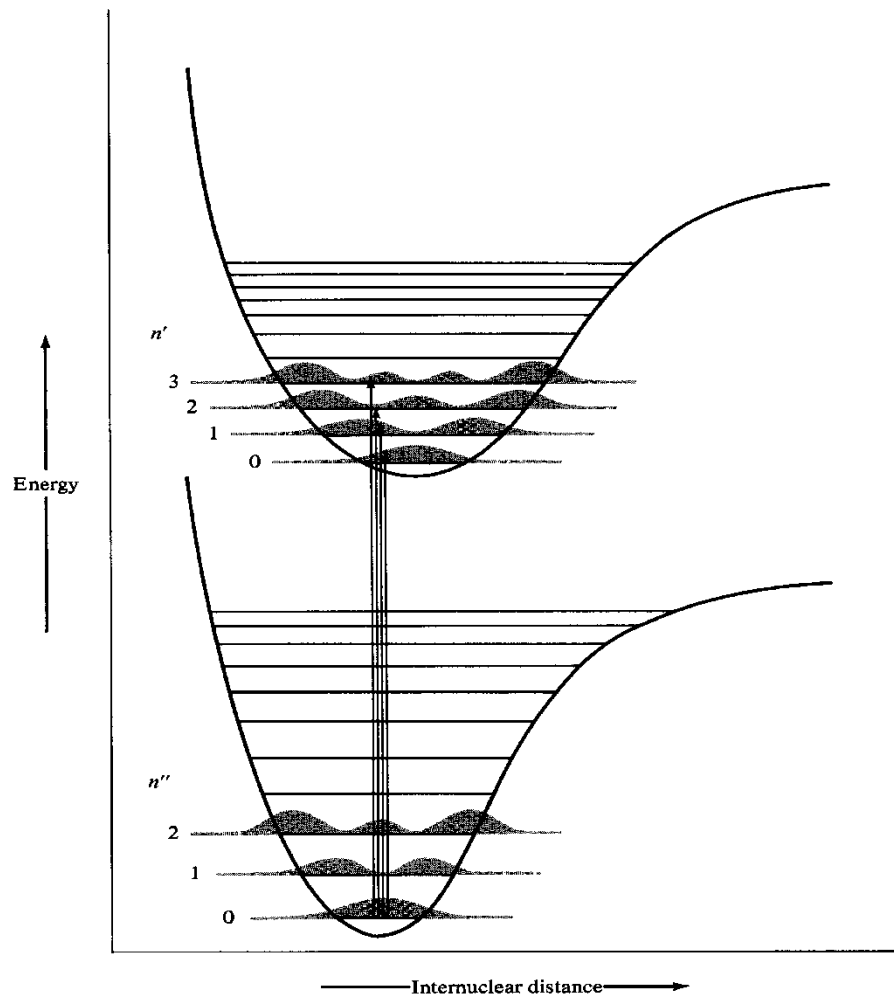
Franck-Condon Principle



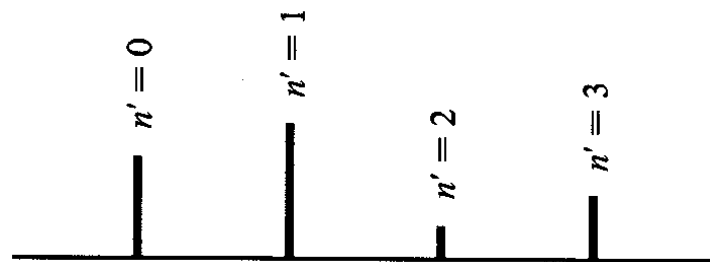
$$I \propto \int S'_{\text{vib}}^* S_{\text{vib}} dR$$

Overlap integral





$$r_e \neq r_e^*$$



0-1 is the most intense

Spectra of Polyatomic Molecules

- The spectra of polyatomic molecules are more complicated than those of atoms or diatomic molecules.
- As with diatomic molecules:
 - Rotational transitions can occur without vibrational or electronic transitions
 - Vibrational transitions can occur without electronic transitions but are generally accompanied by rotational transitions
 - Electronic transitions are accompanied by both vibrational and rotational transitions.

Microwave Spectra of Polyatomic Molecules

- A permanent dipole moment is required for a molecule to produce a microwave spectrum.
- A **symmetric linear** molecule such as acetylene (ethyne) has no permanent dipole moment, and does not have a microwave spectrum.
- **Spherical top** molecules such as CCl_4 and SF_6 are so symmetrical that they cannot have a nonzero permanent dipole moment, and they have no microwave spectrum.
- A **symmetric top** molecule with a permanent dipole moment will have a microwave spectrum.
- A microwave spectrum is always observed for an **asymmetric top** molecule

- **Examples of Linear Molecules:**

carbon dioxide (O=C=O)

no permanent dipole moment

hydrogen cyanide (HC≡N)

carbonyl sulfide (O=C=S)

chloroethyne (HC≡CCl)

acetylene (HC≡CH)

no permanent dipole moment

- **Examples of spherical top molecules:** have no microwave spectrum

methane (CH₄)

phosphorus tetramer (P₄)

carbon tetrachloride (CCl₄)

ammonium ion (NH₄⁺)

uranium hexafluoride (UF₆)

- **Examples of symmetric top molecules:**

benzene (C₆H₆)

no permanent dipole moment

cyclobutadiene (C₄H₄)

no permanent dipole moment

ammonia (NH₃)

chloroform (CHCl₃)

methylacetylene (CH₃C≡CH).

- **Examples of asymmetric top molecules:**

anthracene (C₁₄H₁₀)

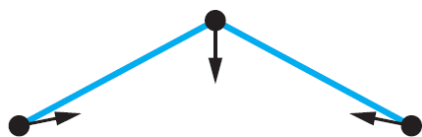
water (H₂O)

nitrogen dioxide (NO₂)

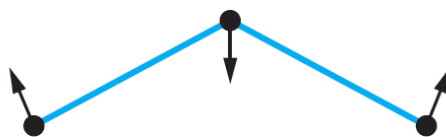
Vibrational Spectra of Polyatomic Molecules

- In the harmonic oscillator approximation the vibration of polyatomic molecules is that of normal modes, each acting like an independent harmonic oscillator
- Number of normal modes are $3n - 5$ for linear molecules and $3n - 6$ for nonlinear molecules
- The selection rules for vibrational transitions are:
 $\Delta v = 0$ or ± 1 for one normal mode, $\Delta v = 0$ for all other normal modes must modulate the molecule's dipole moment
- Transitions obeying $\Delta v = \pm 1$ rule produce *fundamental bands*
- The vibrational selection rules are less well obeyed than the rotational selection rules. There are *overtone bands* in which $\Delta v = 2$ (and sometimes 3), and *combination bands*.

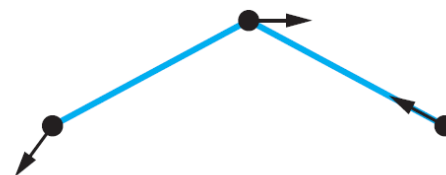
- If a polyatomic molecule possesses a **permanent dipole moment**, all of its normal modes **modulate the dipole** and give rise to **vibrational bands**. For example: SO_2



Symmetric stretch
 $\tilde{\nu}_1 = 1151.2 \text{ cm}^{-1}$

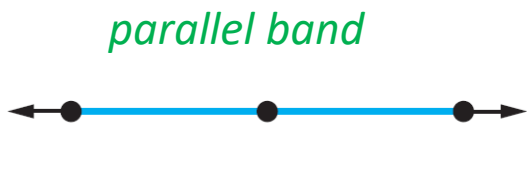


Bend
 $\tilde{\nu}_2 = 519 \text{ cm}^{-1}$

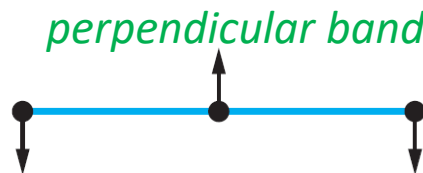


Asymmetric stretch
 $\tilde{\nu}_3 = 1361 \text{ cm}^{-1}$

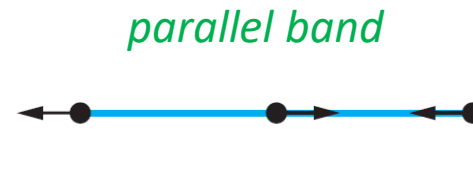
- In molecules **without a permanent dipole**, some of the normal modes can produce a **fluctuating dipole** and thus produce **infrared absorption**. For example, the CO_2



Symmetric stretch
 $\tilde{\nu}_1 = 1340 \text{ cm}^{-1}$



Bend (2 of these)
 $\tilde{\nu}_2 = 667 \text{ cm}^{-1}$



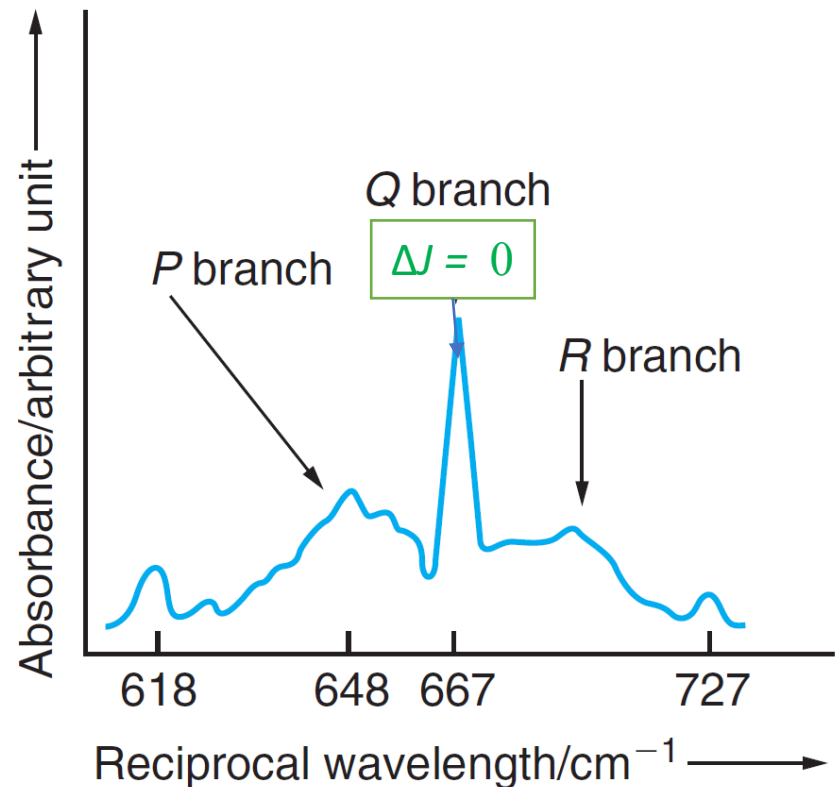
Asymmetric stretch
 $\tilde{\nu}_3 = 2349 \text{ cm}^{-1}$

↓
 No **IR** band

└──────────┘
 produce **IR absorption**

The two bending modes produce a motion in which the center atom moves around in a circle similar to a rotation of a bent molecule, which turns out to permit $\Delta J = 0$ as well as $\Delta J = \pm 1$.

The situation with nonlinear triatomic molecules is similar. Vibrational motions in which the dipole oscillates perpendicular to a single symmetry axis produce a band with a *Q* branch as well as *P* and *R* branches.



Carbon dioxide perpendicular band at 667 cm⁻¹, containing *P*, *Q*, and *R* branches

Electronic Spectra of Polyatomic Molecules

- As with diatomic molecules, vibrational and rotational transitions in polyatomic molecules take place along with electronic transitions.
- Very complicated spectra
- The Franck–Condon principle applies.
- The most important selection rule is the same for all molecules and atoms: The total spin quantum number is the same for the final as for the initial state:

$$\Delta S = 0$$

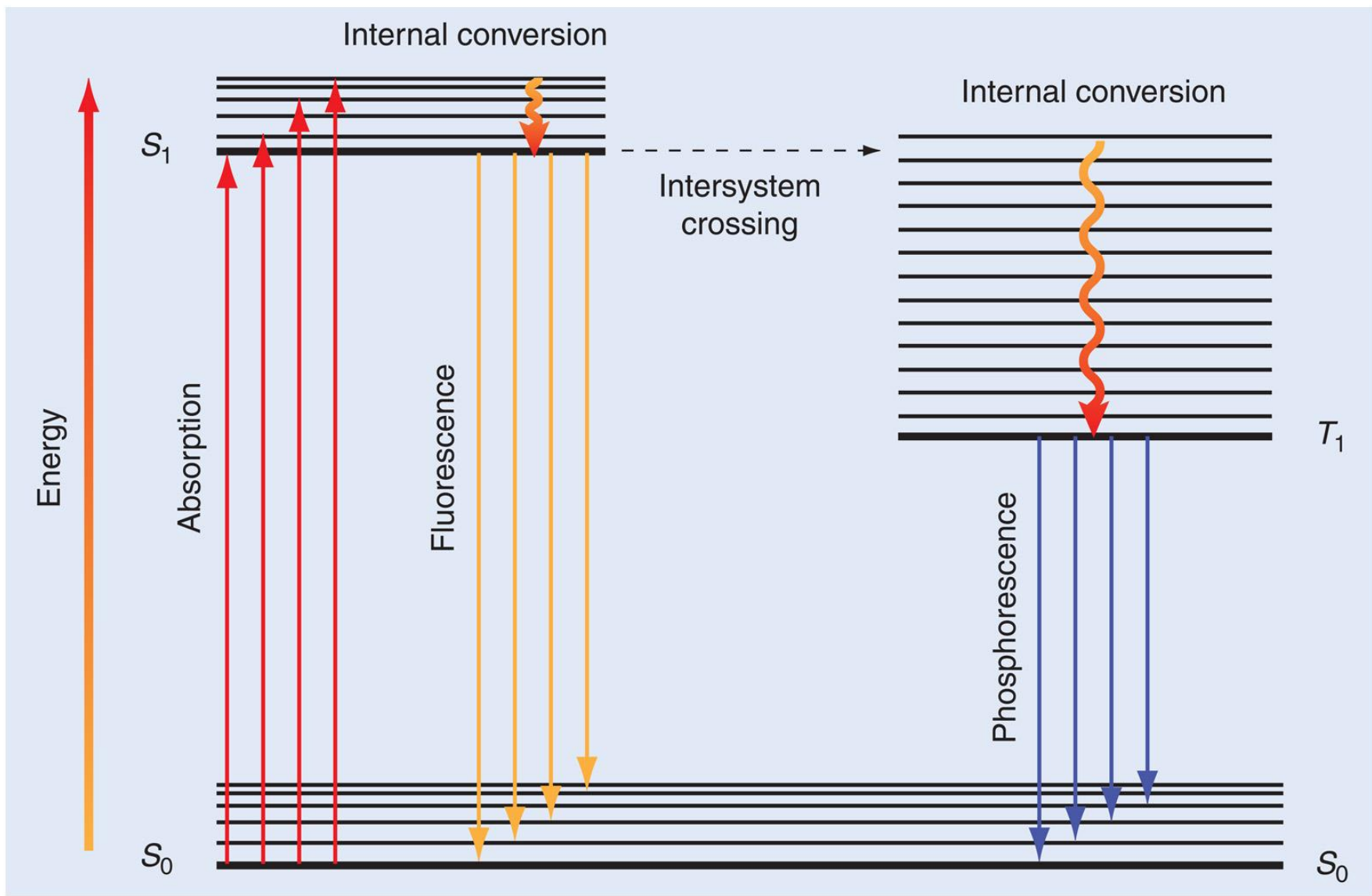
The symmetry of the electronic wave function must change

$(u \rightarrow g \text{ or } g \rightarrow u)$ Allowed
 $(u \rightarrow u \text{ or } g \rightarrow g)$ Forbidden

- “Forbidden” transitions are often observed with low probabilities.
- For example, a transition from an excited **singlet** state to a **singlet** ground state with emission of a photon is **allowed** and will generally occur with a mean lifetime of the excited state of a microsecond to a millisecond. Such a transition is called *fluorescence*.
- A transition from an excited **triplet** state to a **singlet** ground state with emission of a photon is **forbidden**, and if it occurs it will have a smaller intensity and a longer mean lifetime of the excited state (sometimes as long as 10 seconds). Such a transition is called *phosphorescence*.

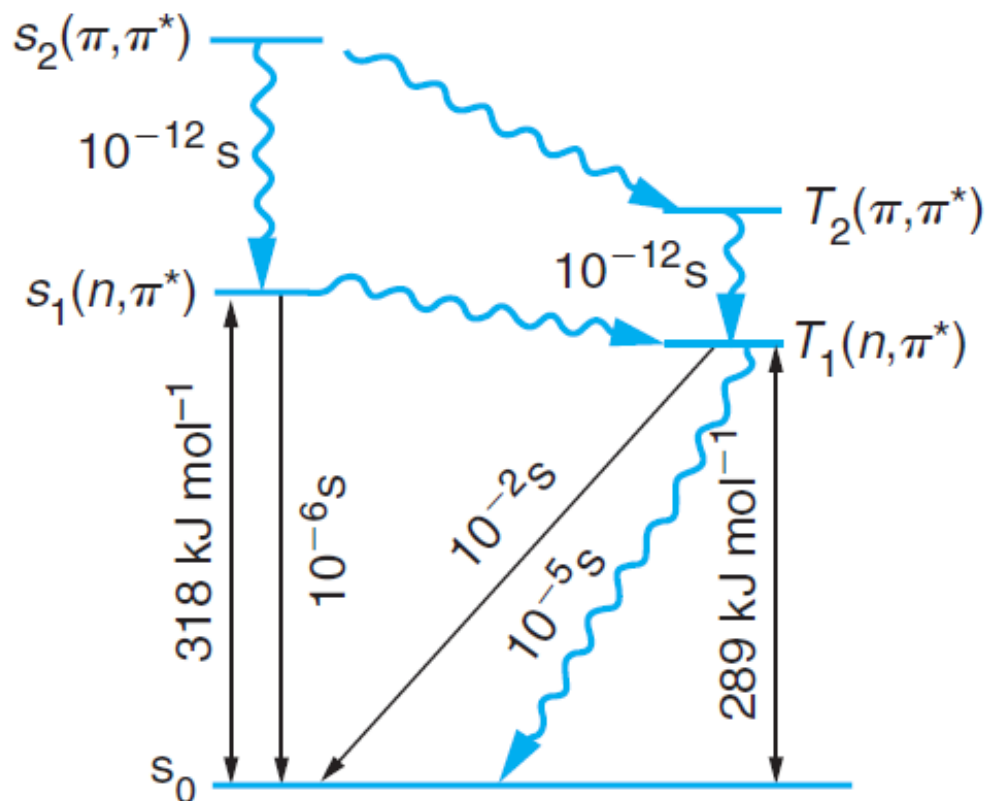
- Transition from a nonbonding orbital to an antibonding π orbital, we call it an n to π^* ($n \rightarrow \pi^*$) transition, and similarly for a π to π^* ($\pi \rightarrow \pi^*$) transition.
- Functional group that exhibits a characteristic absorption is called a *chromophore*.
- For example, most organic compounds containing a carbonyl group have an absorption near **200 nm** corresponding to a $\pi \rightarrow \pi^*$ transition and another absorption near **300 nm** corresponding to an $n \rightarrow \pi^*$ transition.

Fluorescence, Phosphorescence, and Photochemistry



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- A *radiationless transition or internal conversion*: the vibrational energy is transferred to other vibrational modes in the molecule or to rotation or translation of the molecule or to other molecules.



- *Fluorescence*: A radiative transition to the ground level from an excited level with the *same* value of S .

Some Energy Levels of the Benzophenone Molecule.

The wavy arrows represent radiationless transitions, and the straight arrows represent emissions of photons. The times shown are relaxation times for the transitions.

- In fluorescence:
 1. the emitted light will have a longer wavelength than the absorbed light.
 2. Many common objects, including human teeth, certain minerals, and blacklight posters, can fluoresce, emitting visible light after absorbing ultraviolet light.
- *Intersystem Crossing*: is a radiationless transition to an electronic level with a different value of S .
- *Phosphorescence*: A radiative transition to the ground level from an excited level with the *different* value of S
- A typical mean time for phosphorescence is longer than for fluorescence (typically 1 ms to 10 s).



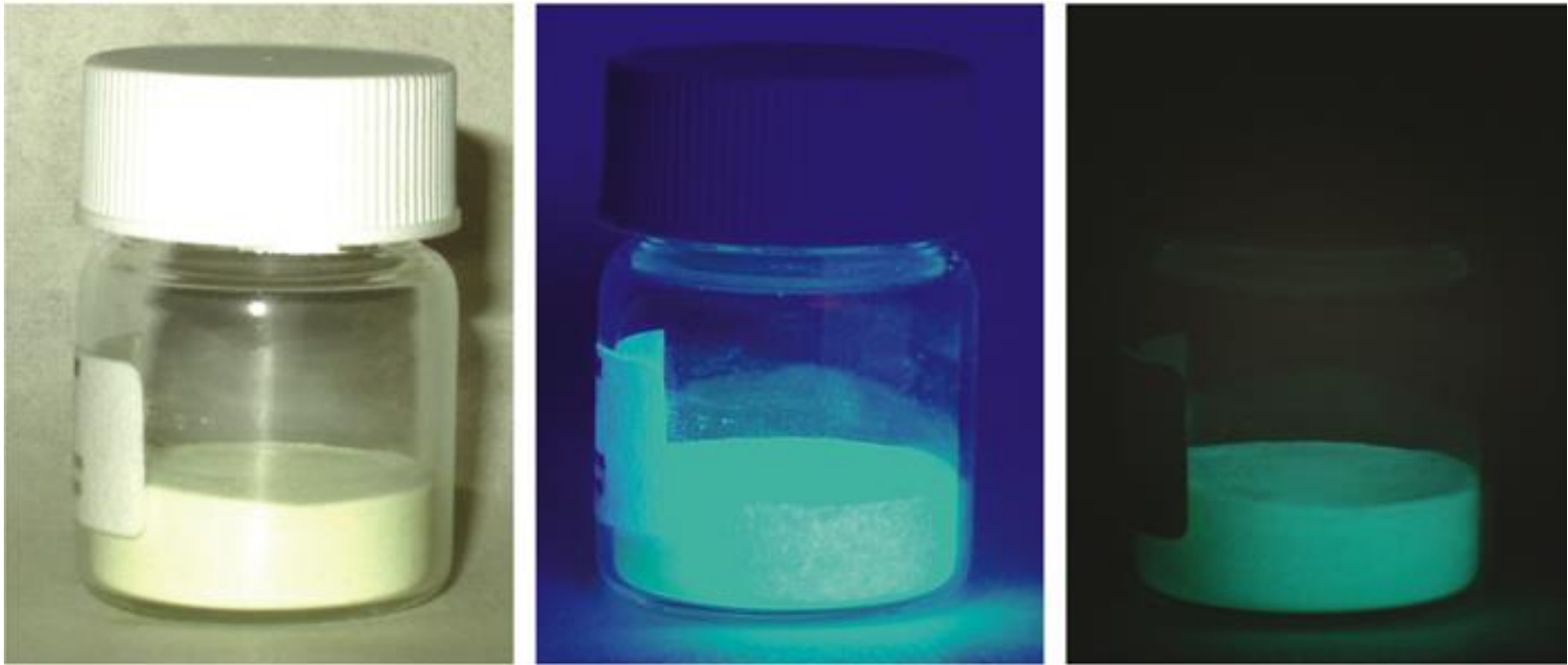
Fluorescent minerals, shown under ultraviolet light



Tonic water is clear under normal light, but vividly fluorescent under ultraviolet light, due to the presence of the quinine used as a flavoring.



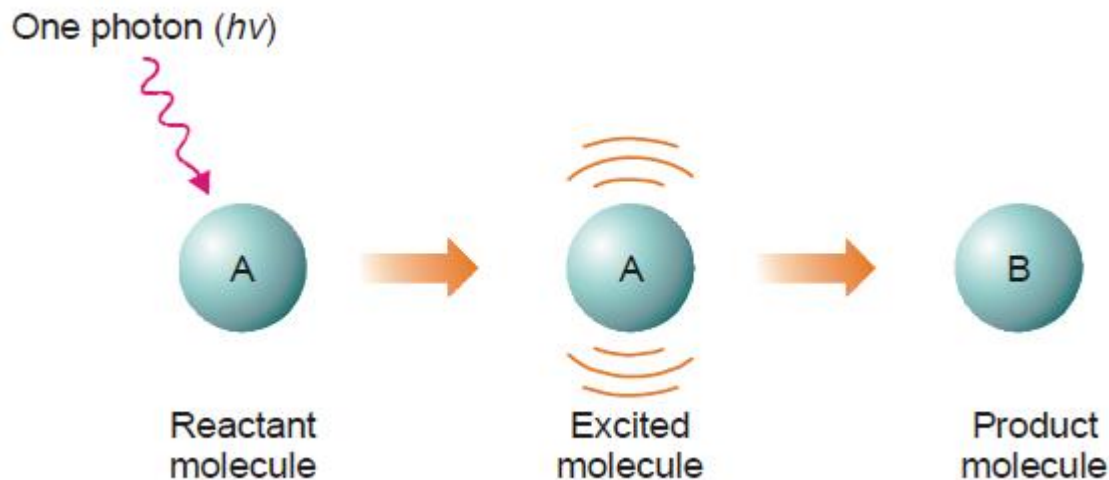
A solution of chlorophyll in ether solution shows blood red fluorescence.



Phosphorescent powder under visible light, ultraviolet light, and total darkness

Photochemistry

- A reaction which takes place by absorption of the visible and ultraviolet radiations is called a *photochemical reaction*.
- Most photochemical reactions are governed by the *Stark–Einstein law of photochemistry*, which states that **absorption of one photon causes the reaction of one molecule.**



- A *chain reaction* might occur in which the reaction of one molecule can lead to the reaction of other molecules without absorption of additional radiation.
- The *quantum yield* of a photochemical reaction, Φ , is defined by

$$\Phi = \frac{\text{number of molecules reacted}}{\text{number of photons absorbed}}$$

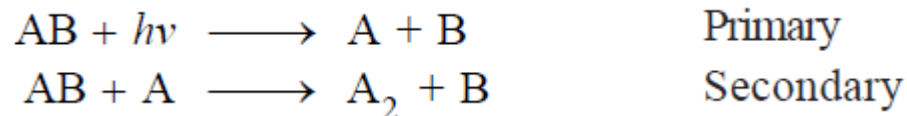
- One mole of photons is called an *einstein*, so that:

$$\Phi = \frac{\text{amount reacted in moles}}{\text{amount of photons absorbed in einsteins}}$$

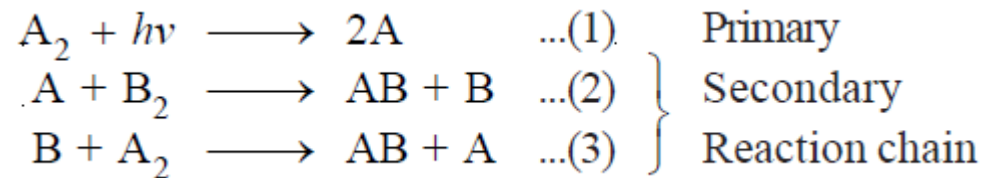
- In a chain reaction, Φ can exceed unity, but in a nonchain reaction, $\Phi \leq 1$.

- **Cause of high quantum yield**

a. **Reactions subsequent to the Primary reaction**

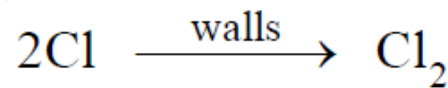
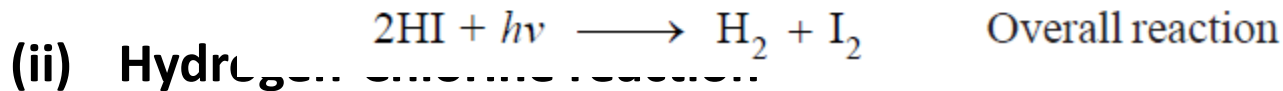
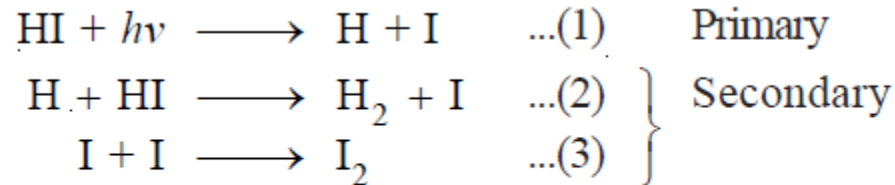


b. **A reaction chain forms many molecules per photon**



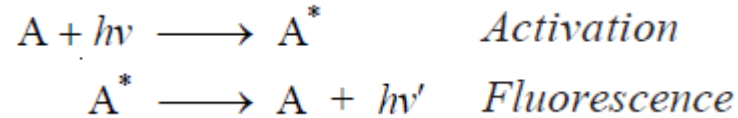
• **Examples of high quantum yield**

(i) Decomposition of HI.

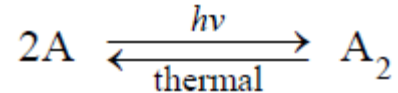


- Causes of low quantum yield

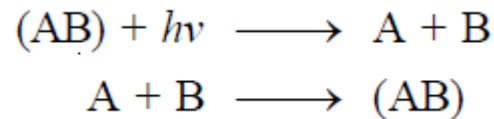
- a) Deactivation of reacting molecules



- b) Occurrence of reverse of primary reaction

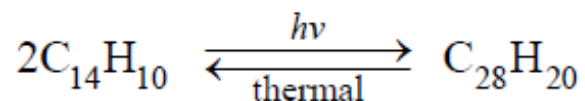
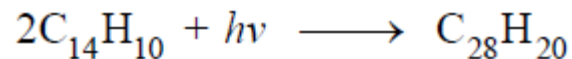


- c) Recombination of dissociated fragments.

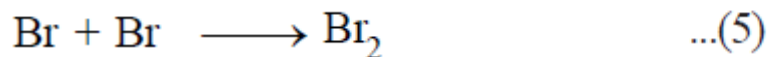
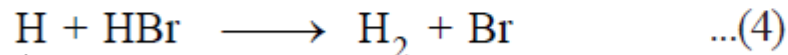
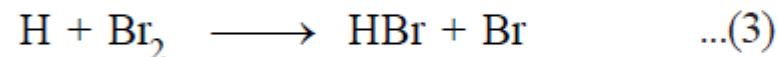
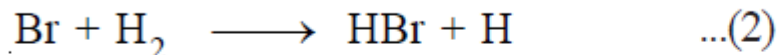


- Examples of low quantum yield

- i. Dimerization of Anthracene



- ii. Combination of H₂ and Br₂



} Secondary reactions

CALCULATION OF QUANTUM YIELD

$$\phi = \frac{\text{Number of molecules decomposed or formed}}{\text{Number of photons of radiation energy absorbed}}$$

$$\phi = \frac{\text{Number of moles decomposed or formed}}{\text{Number of moles of radiation energy absorbed}}$$

The energy of photons; einstein

We know that the energy of a photon (or quantum), ϵ , is given by the equation.

$$\epsilon = h\nu = \frac{hc}{\lambda} \quad \dots(1)$$

where

h = Planck's constant

ν = frequency of radiation

λ = wavelength of radiation

c = velocity of light

If λ is given in cm, the energy is expressed in ergs.

The energy, E , of an Avogadro number (N) of photons is referred to as one einstein. That is,

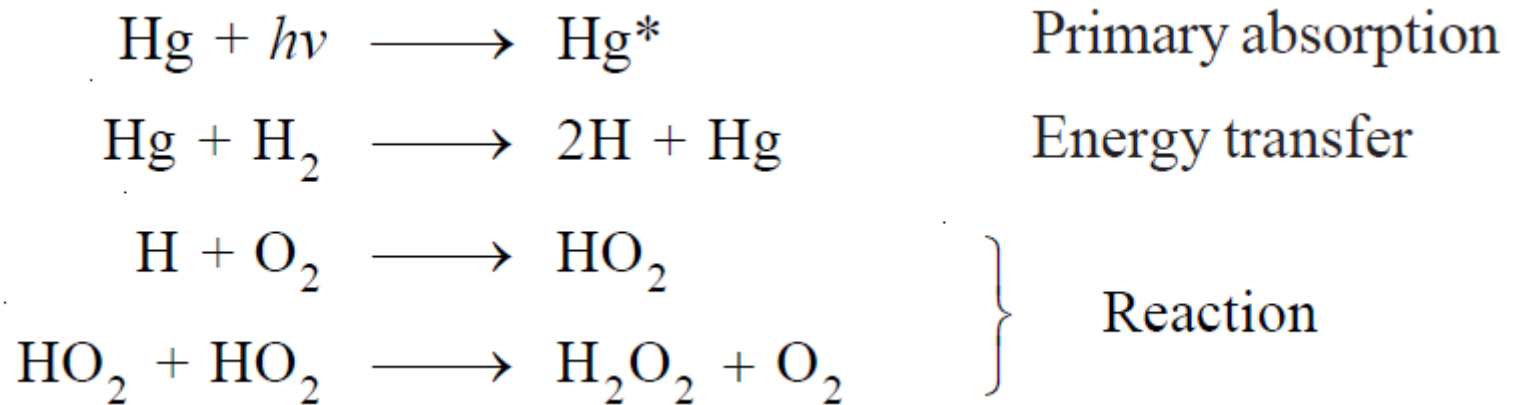
$$E = \frac{Nhc}{\lambda} \quad \dots(2)$$

PHOTOSENSITIZED REACTIONS

species which can both absorb and transfer radiant energy for activation of the reactant molecule, is called a **photosensitizer**

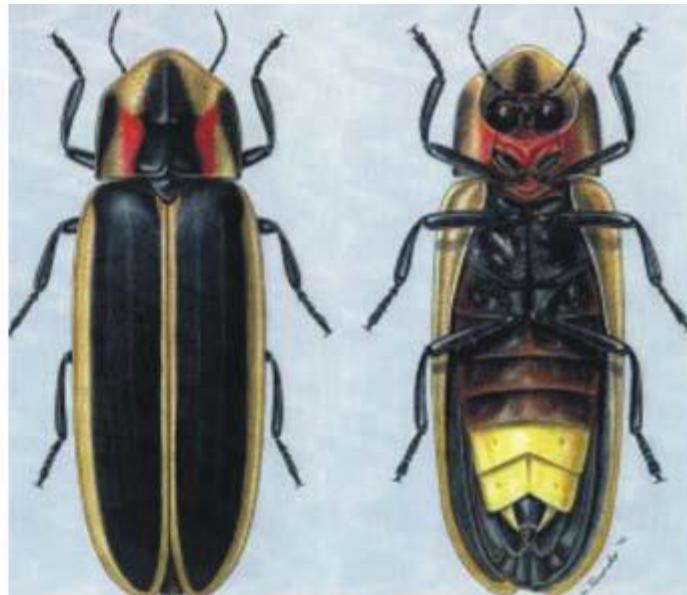
Examples of Photosensitized reactions

Reaction between H_2 and O_2 in presence of Hg



Chemiluminescence

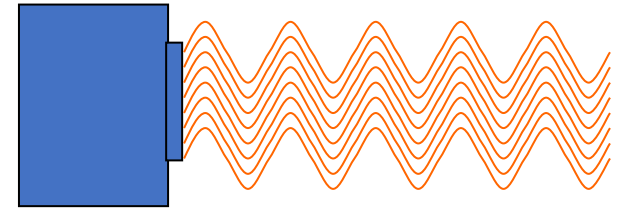
- Some chemical reactions are accompanied by the emission of visible light at ordinary temperature.
- **The emission of light as a result of chemical action is called chemiluminescence.**
- Such a reaction is the reverse of a photochemical reaction which proceeds by absorption of light.
- The light emitted in a chemiluminescent reaction is also called '**cold light**' because it is produced at ordinary temperature.



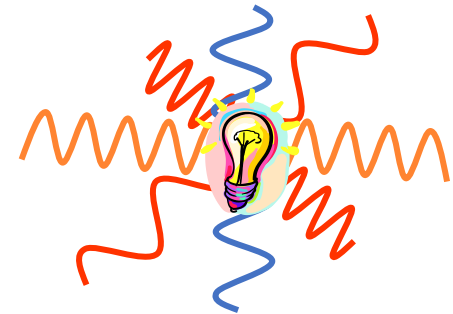
Spectroscopy Application

Laser - Characteristics

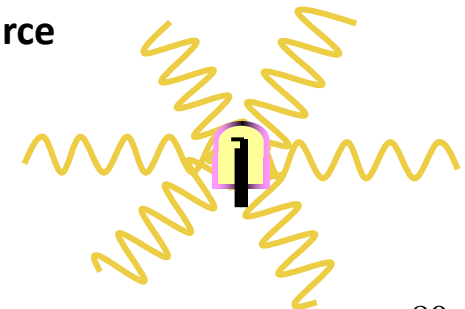
- **Laser - is a special type of light sources or light generators. The word LASER represents Light Amplification by Stimulated Emission of Radiation**
- **Characteristics of light produced by Lasers**
 - **Monochromatic (single wavelength)**
 - **Coherent (in phase)**
 - **Directional (narrow cone of divergence)**

**Incandescent lamp**

- Chromatic
- Incoherent
- Non-directional

**Monochromatic light source**

- Coherent
- Non-directional



The first microwave laser was made in the microwave region in 1954 by Townes & Shawlow using ammonia as the lasing medium.

The first optical laser was constructed by Maiman in 1960, using ruby (Al_2O_3 doped with a dilute concentration of Cr^{+3}) as the lasing medium and a fast discharge flash-lamp to provide the pump energy.

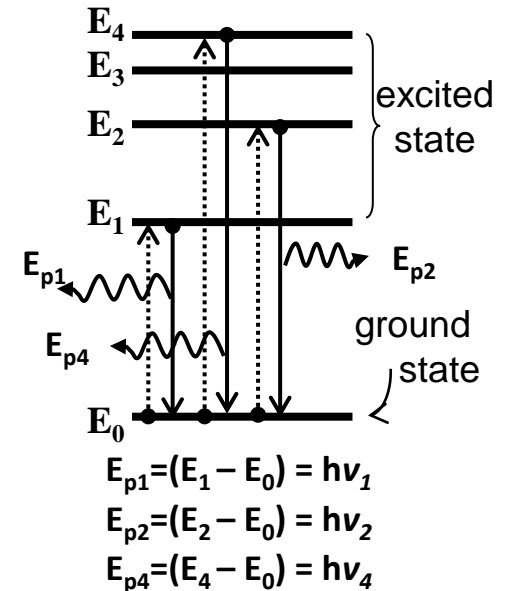
Spectroscopy Application

Laser - Stimulated Emission

- When excited atoms/molecules/ions undergo de-excitation (from excited state to ground state), light is emitted
- Types of light emission

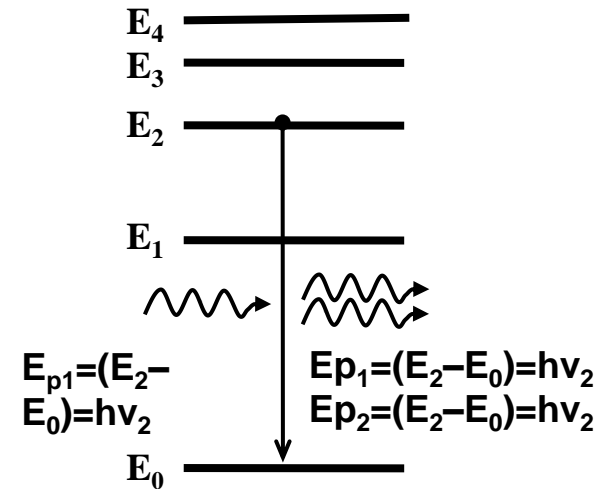
○ *Spontaneous emission* - chromatic & incoherent

- Excited e⁻'s when returning to ground states emit light spontaneously (called *spontaneous emission*).
- Photons emitted when e⁻'s return from different excited states to ground states have different frequencies (chromatic)
- Spontaneous emission happens randomly and requires no event to trigger the transition (various phase or incoherent)



Laser - Stimulated Emission

- Types of light emission (*cont'd*)
 - **Stimulated emission** - monochromatic & coherent
 - While an atom is still in its *excited* state, one can bring it down to its ground state by stimulating it with a photon (P_1) having an energy equal to the energy difference of the excited state and the ground state. In such a process, the incident photon (P_1) is not absorbed and is emitted together with the photon (P_2), The latter will have *the same frequency* (or energy) and *the same phase* (coherent) as the stimulating photon (P_1).



□ Laser uses the stimulated emission process to amplify the light intensity

As in the stimulated emission process, one incident photon (P_1) will bring about the emission of an additional photon (P_2), which in turn can yield 4 photons, then 8 photons, and so on....

Spectroscopy Application

Laser - Formation & Conditions

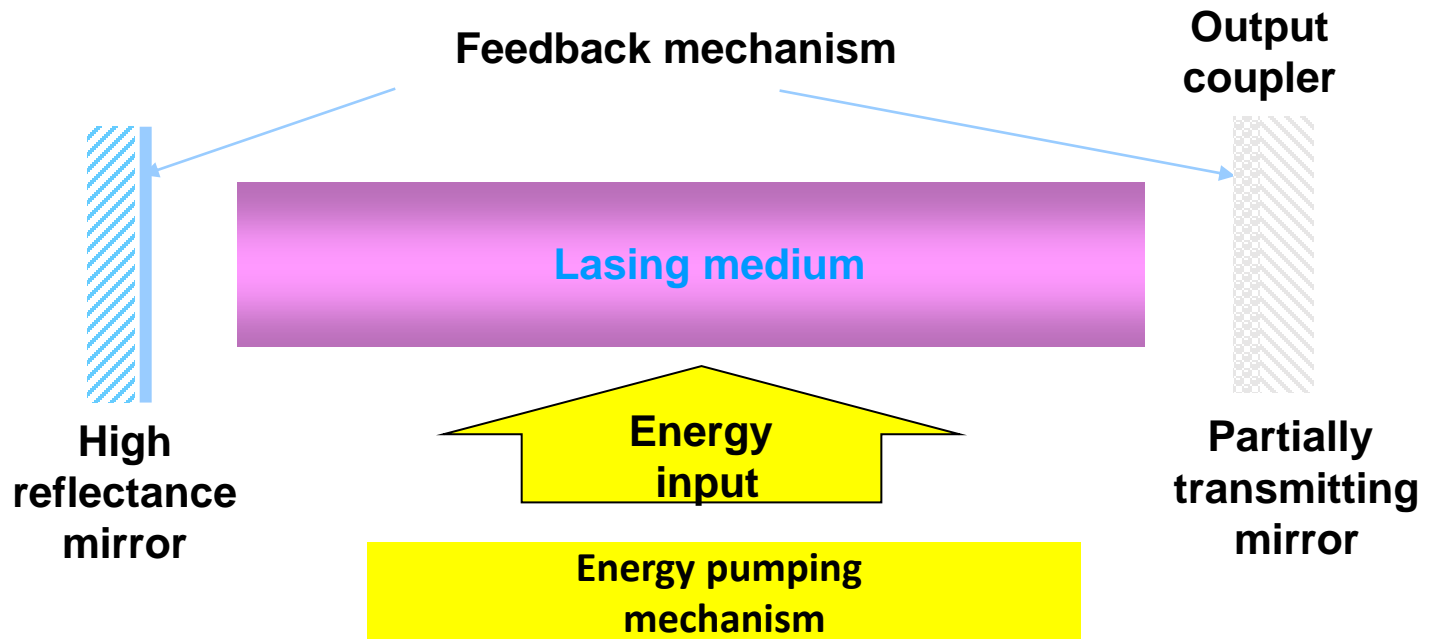
- **The conditions must be satisfied in order to sustain such a chain reaction:**
 - **Population Inversion (PI)**, a situation that there are more atoms in a certain excited state than in the ground state

PI can be achieved by a variety means (electrical, optical, chemical or mechanical), e.g., one may obtain PI by irradiating the system of atoms by an enormously intense light beam or, if the system of atoms is a gas, by passing an electric current through the gas.
 - Presence of **Metastable** state, which is the excited state that the excited e⁻s can have a relatively long lifetime ($>10^{-8}$ second), in order to avoid the spontaneous emission occurring before the stimulated emission

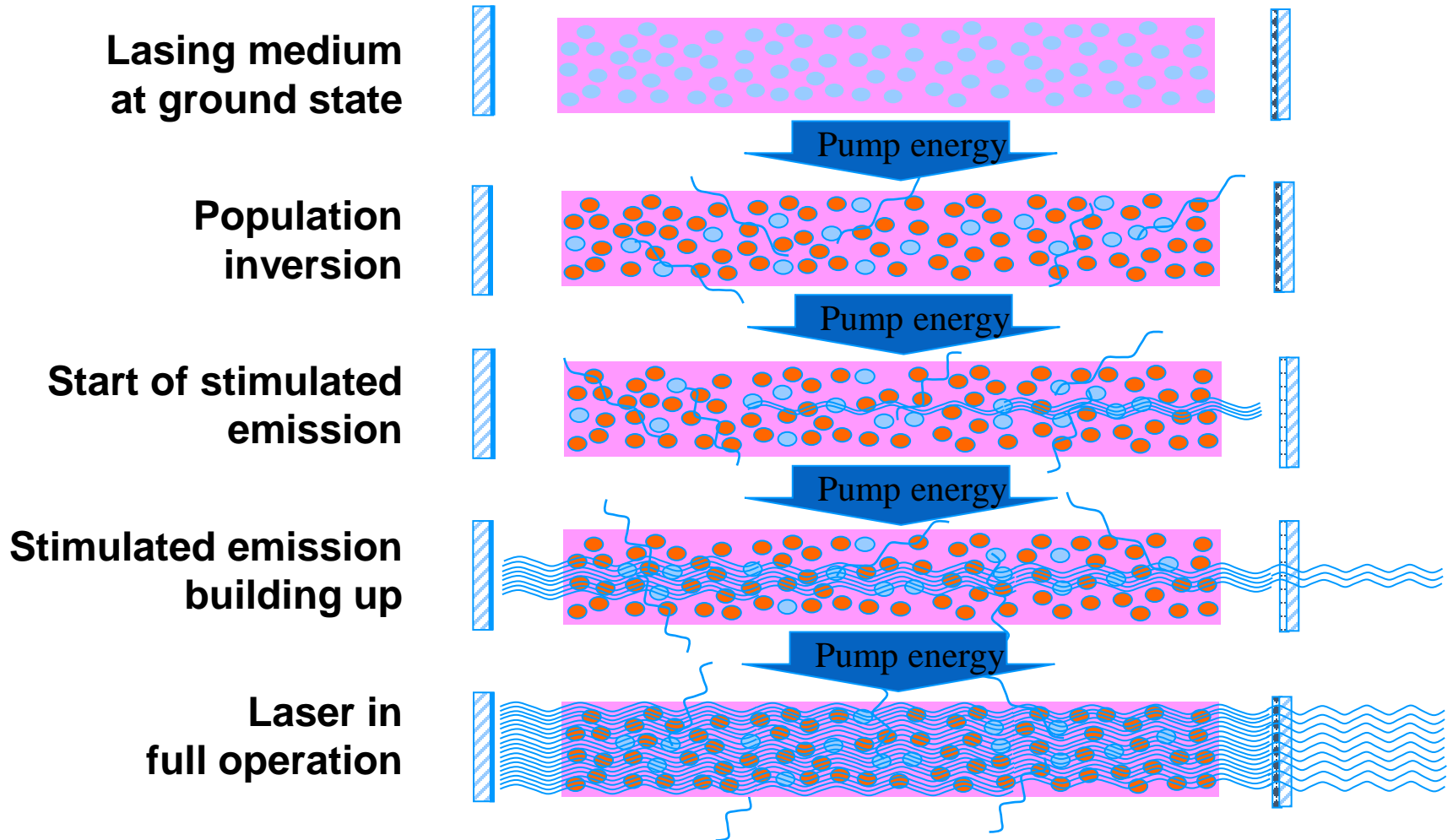
In most lasers, the atoms/molecules/ions in the lasing medium are not “pumped” directly to a metastable state. They are excited to an energy level higher than a metastable state, then drop down to the metastable state by spontaneous non-radiative de-excitation.
 - **Photon Confinement (PC)**, the emitted photons must be confined in the system long enough to stimulate further light emission from other excited atoms

This is achieved by using reflecting mirrors at the ends of the system. One end is made totally reflecting & the other is slight transparent to allow part of the laser beam to escape.

Laser - Functional Elements



Laser Action



Types of Lasers

- There are many different types of lasers
 - The lasing medium can be gas, liquid or solid (insulator or semiconductor)
 - Some lasers produce continuous light beam and some give pulsed light beam
 - Most lasers produce light wave with a fixed wave-length, but some can be tuned to produce light beam of wave-length within a certain range.

Laser type	Physical form of lasing medium	Wave length (nm)
Helium neon laser	Gas	633
Carbon dioxide laser	Gas	10600 (far-infrared)
Argon laser	Gas	488, 513, 361 (UV), 364 (UV)
Nitrogen laser	Gas	337 (UV)
Dye laser	Liquid	Tunable: 570-650
Ruby laser	Solid	694
Nd:Yag laser	Solid	1064 (infrared)
Diode laser	Semiconductor	630-680 86

Laser - Applications

- **Laser can be applied in many areas**

- **Commerce**

Compact disk, laser printer, copiers, optical disk drives, bar code scanner, optical communications, laser shows, holograms, laser pointers

- **Industry**

Measurements (range, distance), alignment, material processing (cutting, drilling, welding, annealing, photolithography, etc.), non-destructive testing, sealing

- **Medicine**

Surgery (eyes, dentistry, dermatology, general), diagnostics, ophthalmology, oncology

- **Research**

Spectroscopy, nuclear fusion, atom cooling, interferometry, photochemistry, study of fast processes

- **Military**

Ranging, navigation, simulation, weapons, guidance, blinding

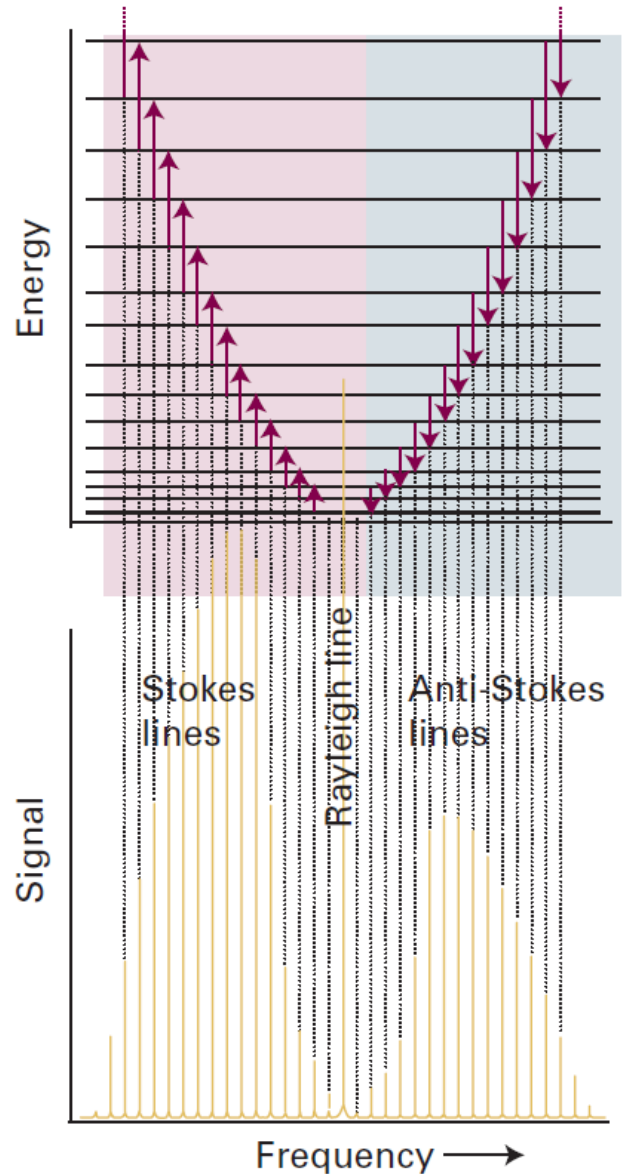
Raman Spectroscopy

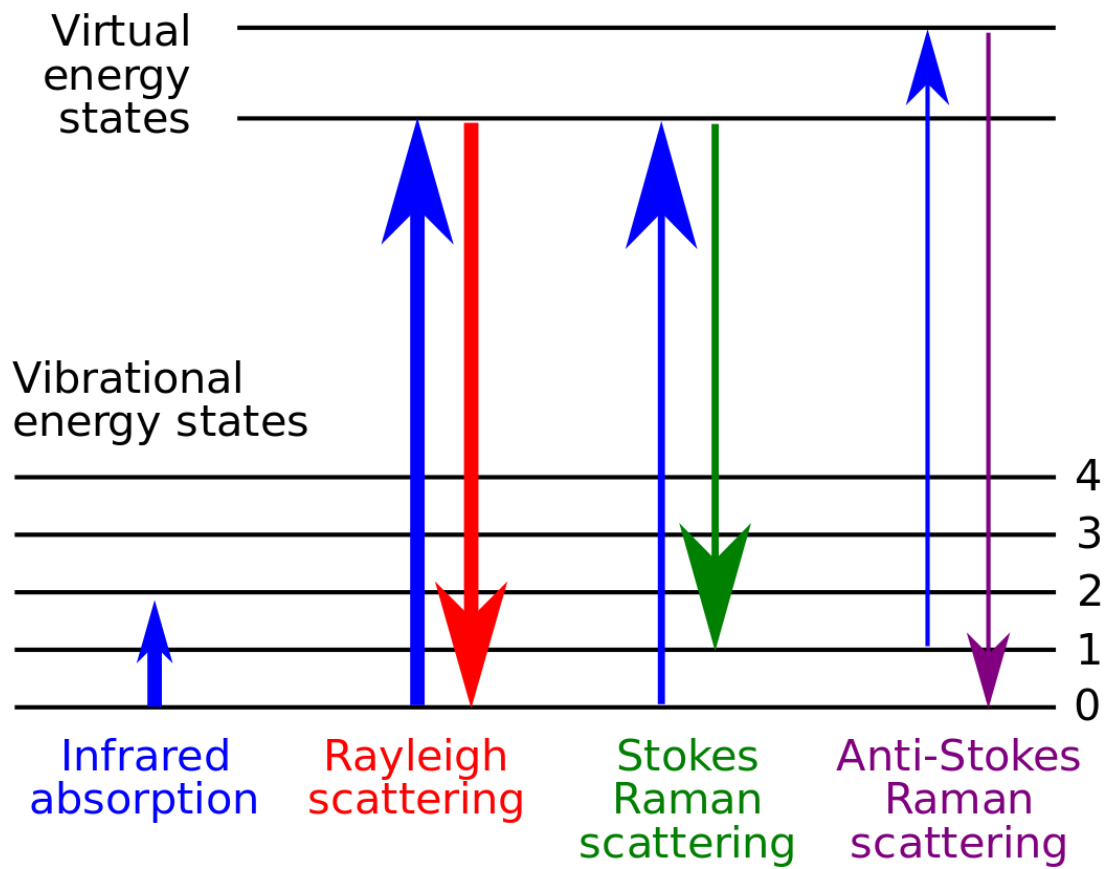
Rayleigh scattering:

- When an intense beam of light is passed through a liquid or gas, some of the light is scattered by the molecules of the medium.
- The scattered light has the same frequency as the incident light.

Raman scattering:

- In 1928, Indian physicist Sir C.V. Raman discovered that a very small fraction of the scattered light has frequencies higher or lower than the incident frequency.
- The scattering which occurs with a change in the frequency of the incident radiation is called The phenomenon is called **Raman effect**.
- The difference between the scattered and incident frequencies or reciprocal wavelengths is called the **Raman shift**





- The difference in the photon energies of the incident and scattered radiation must equal the energy difference between two energy levels of the sample molecules.

$$h\nu - h\nu' = E_{\text{upper}} - E_{\text{lower}}$$

- Spectral lines corresponding to transitions from a lower to a higher molecular energy are called *Stokes lines*, and those corresponding to are called *anti-Stokes lines*.

Explanation of Raman Spectrum:

The change in frequency by scattering occurs due to the exchange of energy between the incident photon and the scattering molecule.

- If the photon collides with an 'excited' molecule, it acquires energy from the molecule. Thus the scattered light emerges with a higher frequency.
- If the photon collides with a molecule in the 'ground state', it loses energy to the molecule. This lowers the frequency of the scattered light.

- The Raman frequencies are independent of the incident frequency and are characteristic of the substance.

- The selection rules for Raman transitions are different from those of absorption or emission, and this makes it possible to observe transitions that are forbidden in emission or absorption spectroscopy.

$$\Delta J = 0, \pm 2 \quad (\text{linear molecules})$$

$$\Delta J = 0, \pm 1, \pm 2 \quad (\text{nonlinear molecules})$$

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

The nuclear motion must modulate the polarizability of the molecule.

The *polarizability* is a measure of the tendency of a molecule to acquire an electric dipole in the presence of an electric field

$$\mu_{\text{ind}} = \alpha \mathcal{E} \quad (\text{isotropic molecule})$$

Raman Spectra and Molecular Structure

Raman spectra provide valuable information about the shape and structure of molecules.

When studied together, Raman and *IR* spectra can tell us whether:

- (i) a molecule is linear or non-linear;
- (ii) a molecule is symmetrical or asymmetrical.

Rotational Raman Spectra

- The rotation of a diatomic or linear polyatomic molecule will be *Raman active* .
- In a nonlinear polyatomic molecule:
 1. A spherical top molecule has no rotational Raman spectrum.
 2. Symmetric tops and asymmetric tops produce rotational Raman spectra.

Vibrational Raman Spectra

Rule of mutual exclusion:

In a molecule with a center of symmetry, a normal mode that is seen in the infrared spectrum will not be seen in the Raman spectrum, and vice versa.

EXAMPLE 13

Figure 19 shows the rotational Raman spectrum of carbon dioxide. From the splitting between the lines, 3.09 cm^{-1} , calculate the equilibrium bond lengths.

Solution

Since the carbon nucleus is at the center of mass and since the two bond lengths are equal to each other the two equal moments of inertia are

$$I_B = I_C = 2m_{\text{O}}r_e^2$$

where r_e is the bond length and m_{O} is the oxygen nuclear mass, $2.656 \times 10^{-26} \text{ kg}$. The parameter \tilde{B} is given by

$$\tilde{B} = \frac{h}{8\pi^2 I_{BC}} = \frac{h}{8\pi^2 2m_{\text{O}}r_e^2 c}$$

Since the selection rule requires that $\Delta J = \pm 2$, the Raman shift for the Stokes lines is given by

$$\begin{aligned}\Delta\tilde{\nu} &= \tilde{\nu} - \tilde{\nu}' = \tilde{B}[(J+2)(J+3) - J(J+1)] = \tilde{B}[J^2 + 5J + 6 - J^2 - J] \\ &= \tilde{B}[4J + 6]\end{aligned}$$

The ^{16}O nuclei are bosons ($I = 0$) and the electronic ground state is a sigma state, so only even values of J can occur. The first spectral line should occur at $6\tilde{B}$, and the splitting between lines should equal $8\tilde{B}$. The first full line that is visible in the figure is the second line, corresponding to the transition from $J = 2$ to $J = 4$. The splitting is found to be 3.09 cm^{-1} by measurement in the figure. Using the symbol $\Delta\tilde{\nu}$ for the splitting, we obtain

$$\begin{aligned}r_e^2 &= \frac{h}{2\pi^2 m_{\text{O}} c \Delta\tilde{\nu}} \\ &= \frac{6.6261 \times 10^{-34} \text{ J s}}{2\pi^2 (2.656 \times 10^{-26} \text{ kg})(3.09 \text{ cm}^{-1})(2.9979 \times 10^{10} \text{ cm s}^{-1})} \\ &= 1.364 \times 10^{-20} \text{ m}^2 \\ r_e &= 1.17 \times 10^{-10} \text{ m} = 117 \text{ pm} = 1.17 \text{ \AA}\end{aligned}$$

This result agrees fairly well with the accepted value, 116.15 pm.

Other Types of Spectroscopy

Photoelectron Spectroscopy

- In this technique ultraviolet radiation is absorbed by a molecule, causing ejection of an electron:



- The kinetic energy of the ejected electron is measured, and the difference in energy between a photon of the incident radiation and the kinetic energy of the electron is taken to be the ionization energy of the ejected electron.
- According to *Koopman's theorem* the ionization energy is equal to the magnitude of the orbital energy of the orbital from which the electron came.

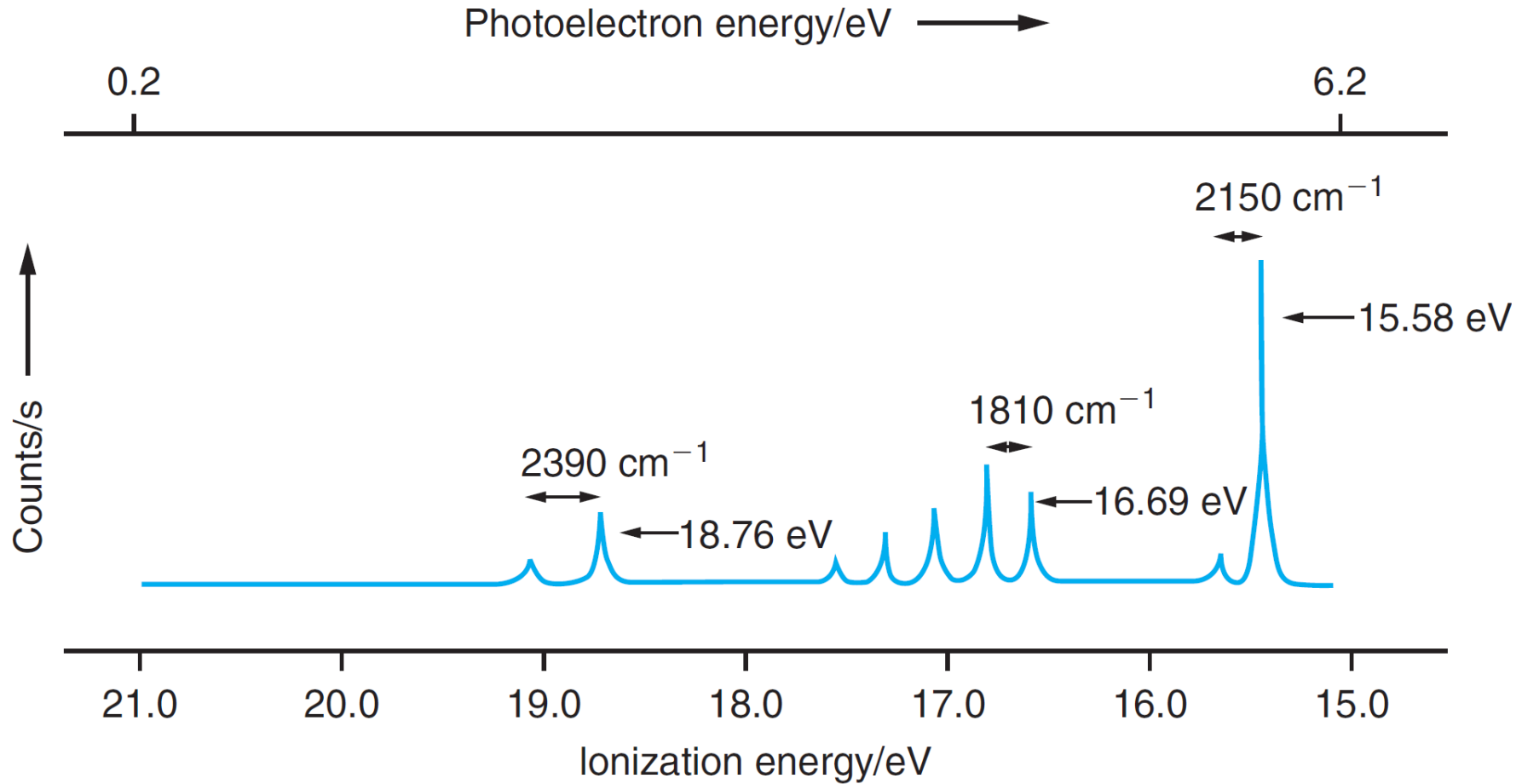


Figure 20 Photoelectron Spectrum of Nitrogen. From I. N. Levine, *Molecular Spectroscopy*, Wiley, New York, 1975, p. 316.

EXAMPLE 14

The ground-state vibrational frequency for nitrogen is 2359 cm^{-1} . The spacing between the lines in the rightmost set of lines corresponds to 2150 cm^{-1} , and the line for the transition from $v = 0$ to $v = 0$ is at 15.58 eV . Find the ionization energy from the minimum of the ground-state potential curve to the minimum in the ion curve.

Solution

The ionization energy from the $v = 0$ vibrational state to the $v = 0$ vibrational state differs from the desired quantity by the difference of the zero-point vibrational energies, given by

$$\begin{aligned}\Delta E_{\text{zero-point}} &= \frac{h\nu_{\text{molecule}}}{2} - \frac{h\nu_{\text{ion}}}{2} = \frac{hc}{2}(\tilde{\nu}_{\text{molecule}} - \tilde{\nu}_{\text{ion}}) \\ &= \frac{(6.6261 \times 10^{-34} \text{ J s})(2.9979 \times 10^{10} \text{ cm s}^{-1})}{2}(209 \text{ cm}^{-1}) \\ &= 2.08 \times 10^{-21} \text{ J} = 0.0130 \text{ eV} \\ \Delta E_{\text{e-e}} &= \Delta E_{0-0} + 0.013 \text{ eV} = 15.58 \text{ eV} + 0.013 \text{ eV} = 15.59 \text{ eV}\end{aligned}$$