Chapter 13. Spectroscopy 2: electronic transitions

-The characteristics of electronic transitions

-The fates of electronically excited states

-Lasers

-Photoelectron spectroscopy

Table 13.1* Colour, frequency, and energy of light

Colour	λ/nm	$\nu/(10^{14}\,\text{Hz})$	$E/(\text{kJ mol}^{-1})$
Infrared	>1000	<3.0	<120
Red	700	4.3	170
Yellow	580	5.2	210
Blue	470	6.4	250
Ultraviolet	<300	>10	>400

* More values are given in the *Data section*.

1 eV = 100 kJ/mol = 8000 cm^{-1}

The characteristics of electronic transitions

• Due to electronic transition, the molecule may respond by starting to vibrate and accompany rotational structure.

13.1 Measurement of intensity

13.2 The electronic spectra of diatomic molecules

13.3 The electronic spectra of polyatomic molecules

The absorption spectrum of chlorophyll in the visible region. Note that it absorbs in the red and blue regions, and that green light is not absorbed appreciably.
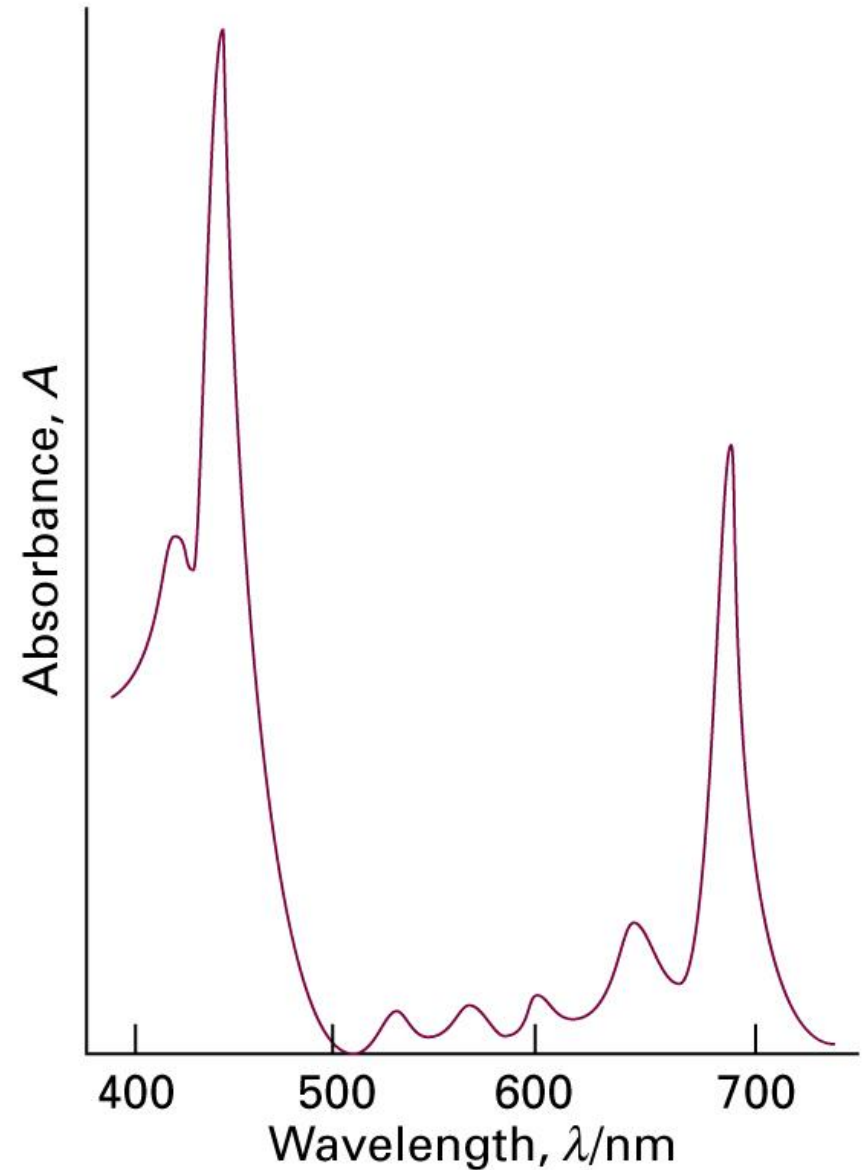
13.1 Measurements of intensity

-Beer-Lambert law

$$I = I_0 10^{-\varepsilon[J]L}$$

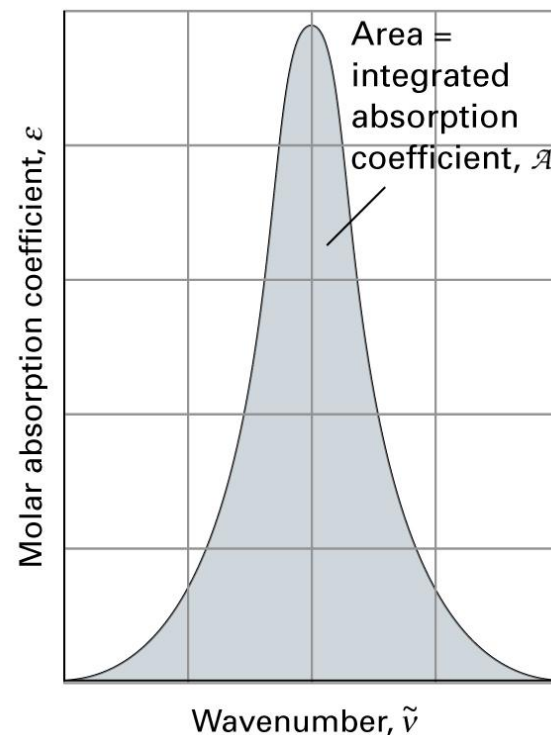$$dI = -\kappa[J]IdL$$

$$\frac{dI}{I} = -\kappa[J]dL$$

$$\int_{I_0}^{I} \frac{dI}{I} = -\kappa \int_{0}^{L} [J]dL$$

-Transmittance $\quad T = \dfrac{I}{I_0}$

-Absorbance $\quad A = \log \dfrac{I_0}{I}$

-integrated absorption coefficient

$$A = \int_{band} \varepsilon[\overline{v}]d\overline{v}$$

Area = integrated absorption coefficient, $\mathcal{A}$

Molar absorption coefficient, ε

Wavenumber, $\tilde{v}$

13.2 The electronic spectra of diatomic molecules

-vibronic transition:
> vib structure in electronic spectra

-**parity** (of an orbital) : behavior under inversion

even (g) if its wavefunction is unchanged under inversion through the centre of symmetry of the molecule

odd (u) if the wavefunction changes sign.

note) Heteronuclear diatomic molecules do not have a centre of inversion, so for them the g, u classification is irrelevant.

Centre of inversion

σ_g

σ_u

π_u

π_g
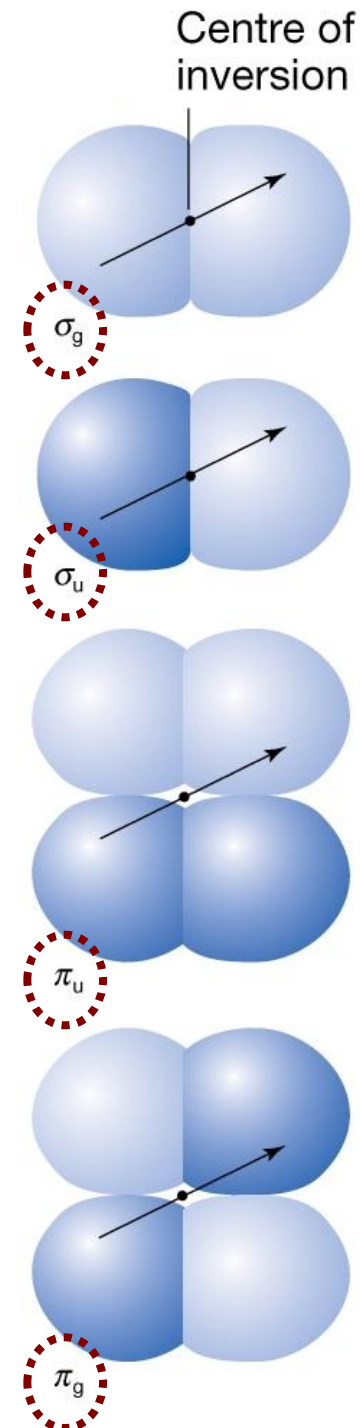
Term symbols [1]

$$\Lambda\hbar$$

the total angular momentum
(orbital and spin) along the internuclear axis

$$|\Lambda| = \Sigma, \Pi, \Delta\ldots$$

$$|\Lambda| = 0, 1, 2, \ldots$$

Λ the sum of the values of λ of individual electrons in a molecule

ex. single electron in a σ orbital has $\lambda = 0$.
the term symbol for H_2^+: Σ

Term symbols [2]

spin multiplicity: 2S+1, S=1/2

-including parity,

for H_2^+: $^2\Sigma_g$

-for gnd state of any closed shell homonuclear diatomic molecule:

$$^1\Sigma_g$$

if there are several electrons, (g as +1, u as -1)
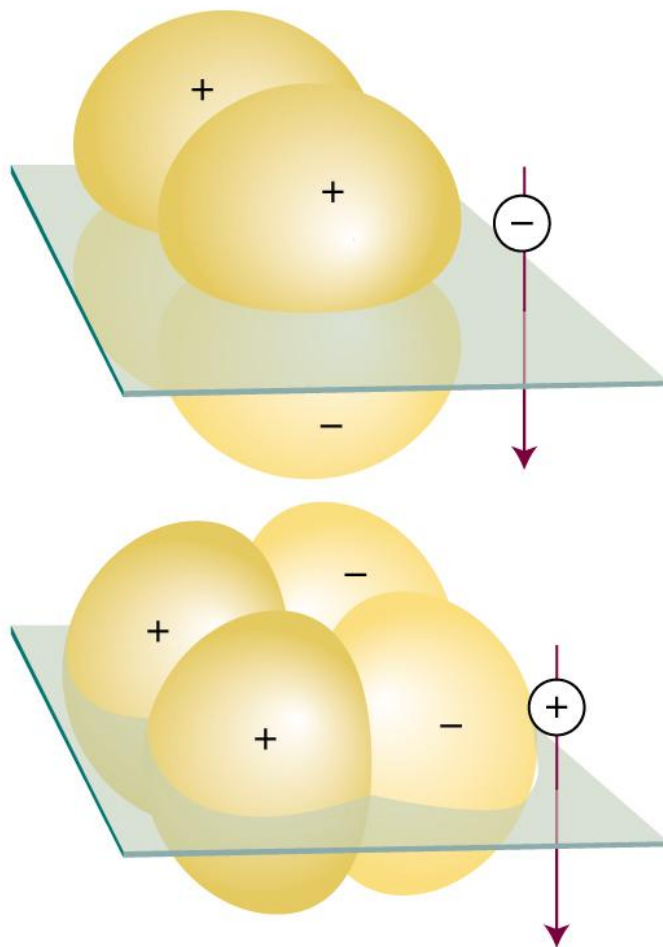gxg=g   uxu=u   uxg=u

Term symbols [3]

-π electron in a diatomic molecule, $\lambda = \pm 1$

-if there are two π electrons, the term symbol will be

Σ if the two e- travels opposite direction
(the different orbital, $\lambda=+1$ and $\lambda=-1$)

Δ if the two e- travels same direction
(the same orbital, both $\lambda=+1$)

for O_2, $\quad \pi_u^2 \pi_u^2 \pi_g^1 \pi_g^1$

(closed shell)xgxg=g $\quad {}^3\Sigma_g$

+ or − subscript
~the overall symmetry of
a configuration of
molecular wavefunction
under reflection in a plane
containing the nuclei.

full term symbol of the ground state of O_2, $\longrightarrow$ $^3\Sigma_g^-$

one electron in $2\pi_x$ (changing sign inder reflection in the yz plane)

one electron in $2\pi_y$ (*not* changing sign inder reflection in the yz plane)

For excited state of oxygen, $^1\Delta_g$

two electrons in the same orbital $\left|\Lambda\right| = 2$

spin is zero… (all electrons are paired)

Selection rules (conservation of angular momentum)

$$\Delta\Lambda = 0, \pm 1 \qquad \Delta S = 0, \qquad \Delta\Sigma = 0, \qquad \Delta\Omega = 0$$

$$\Omega = \Lambda + \Sigma$$ the total angular momentum (orbital and spin)
along the internuclear axis

• two selection rules

   $$\Sigma^+ \leftrightarrow \Sigma^+, \ \ \Sigma^- \leftrightarrow \Sigma^-$$ are allowed.

   Laporte selection rule for centrosymmetric molecules:

   The only allowed transitions are transitions that are
   accompanied by a change of parity
   (u←g and g←u are allowed. g←g and u←u are forbidden)
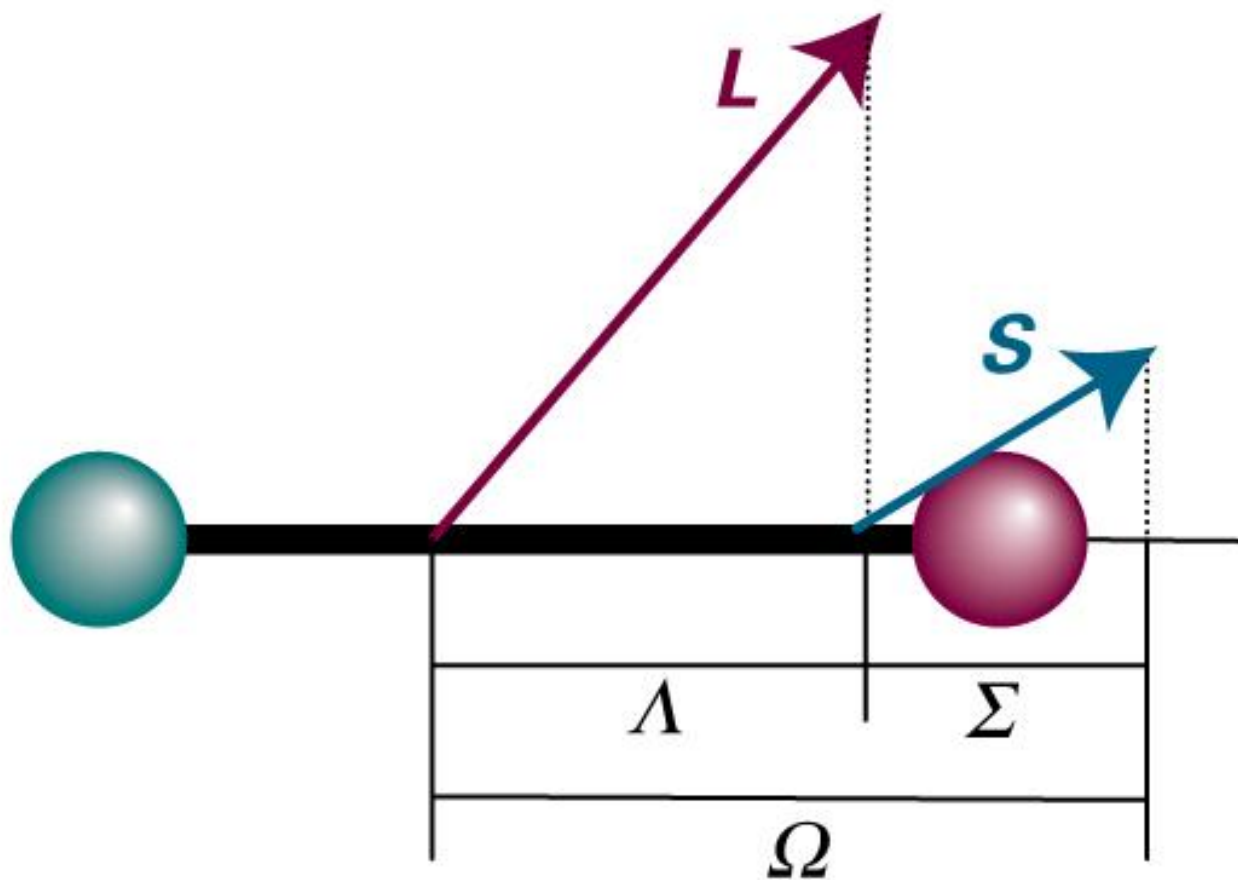
- The coupling of spin and orbital angular momenta in a linear molecule: only the components along the internuclear axis are conserved.

BUT,…

•A d-d transition is
parity-forbidden
(g-g transition)

•However,
a vibration of the molecule can
destroy the inversion symmetry
of the molecule and the g,u
classification no longer applies.

•The removal of the centre of
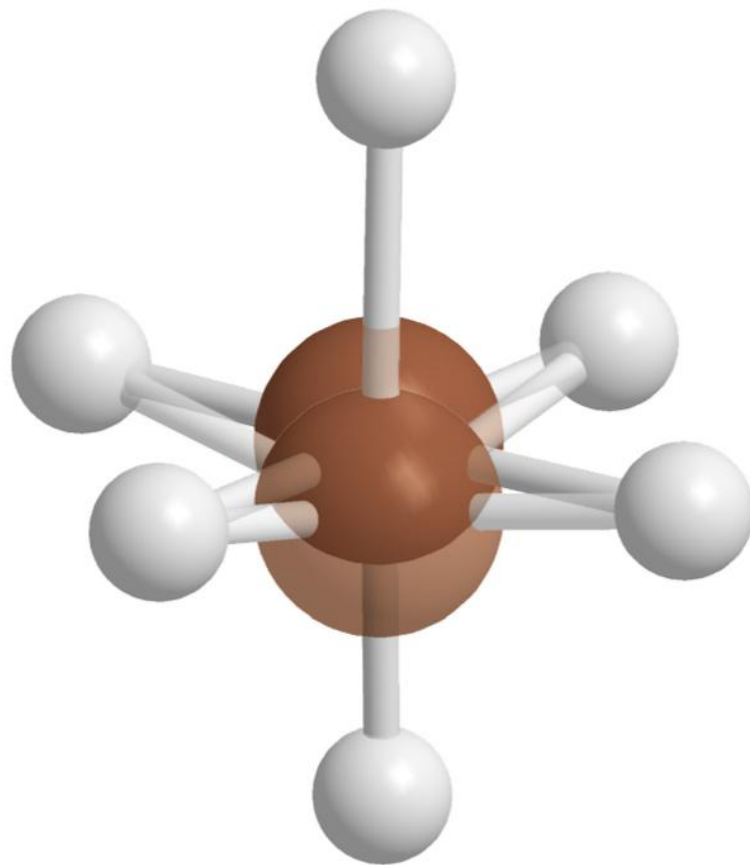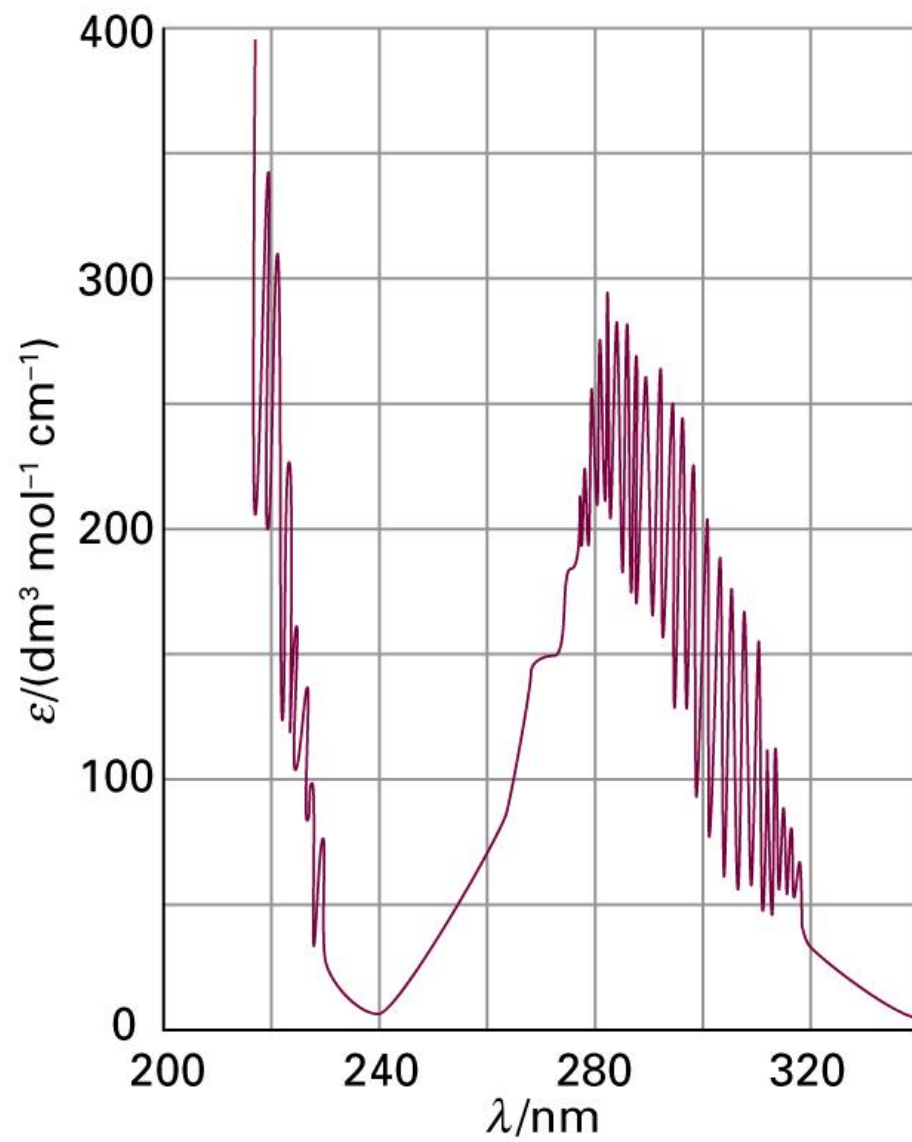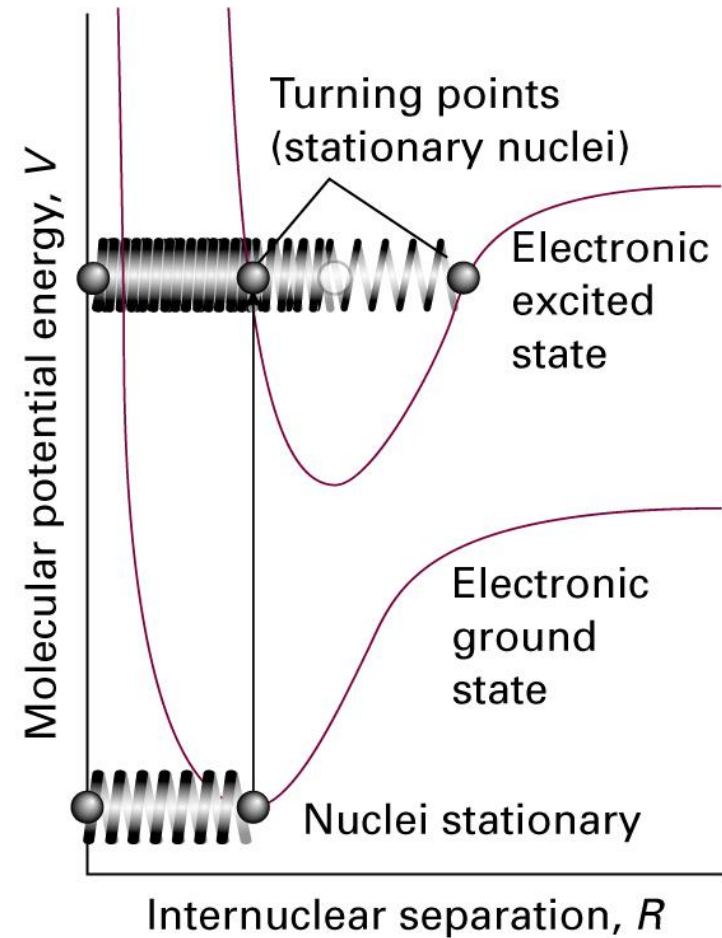symmetry gives rise to a vibronically
allowed transition.

Figure 13.6

Vibrational structure

Franck-Condon principle:
an e- transition is much faster than the
nuclei can respond
(e- is much lighter than nuclei)

- the **most intense vibronic transition** is
  from the ground vibrational state the
  vibrational state lying **vertically above** it.

- Transitions to other vibrational levels also
  occur, but with lower intensity.

•quantum mechanically,

Electronic
excited
state

Electronic
ground
state

R_e Nuclei stationary

Molecular potential energy, V

Internuclear separation, R

•The two wavefunctions have
the **greatest overlap integral**
of all the vibrational states of the
upper electronic state
(hence are most closely similar).
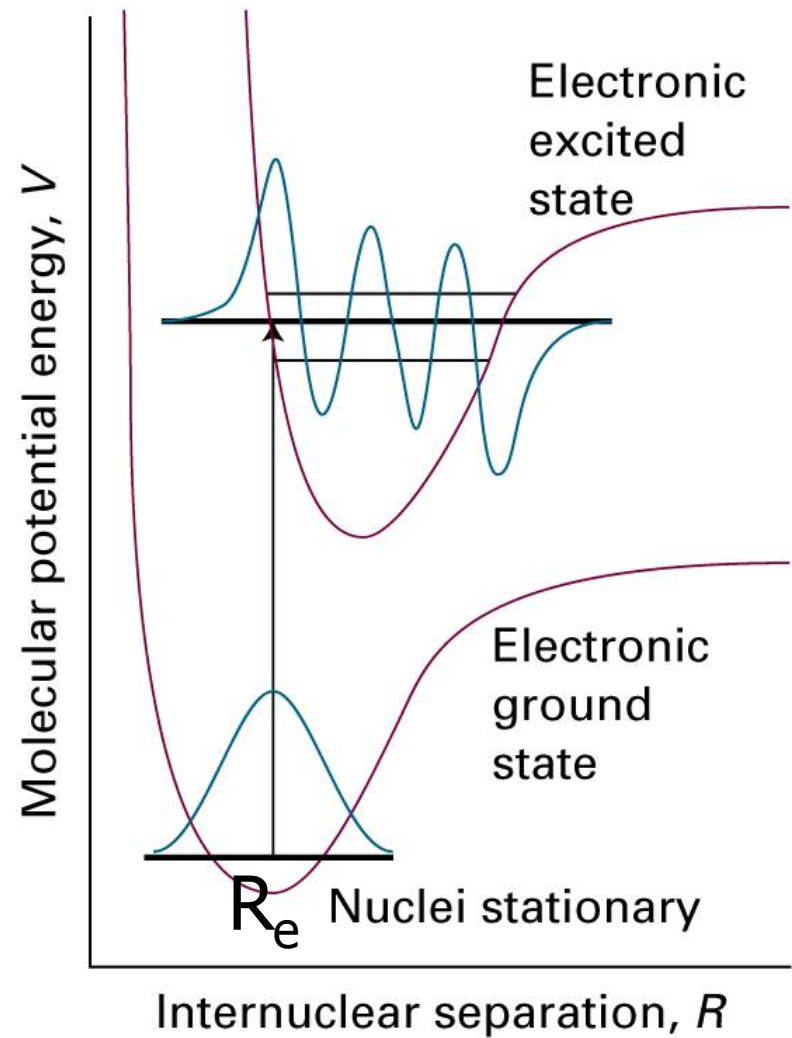
Frank-Condon factors

$$\mu_{fi} = \langle f | \mu | i \rangle$$
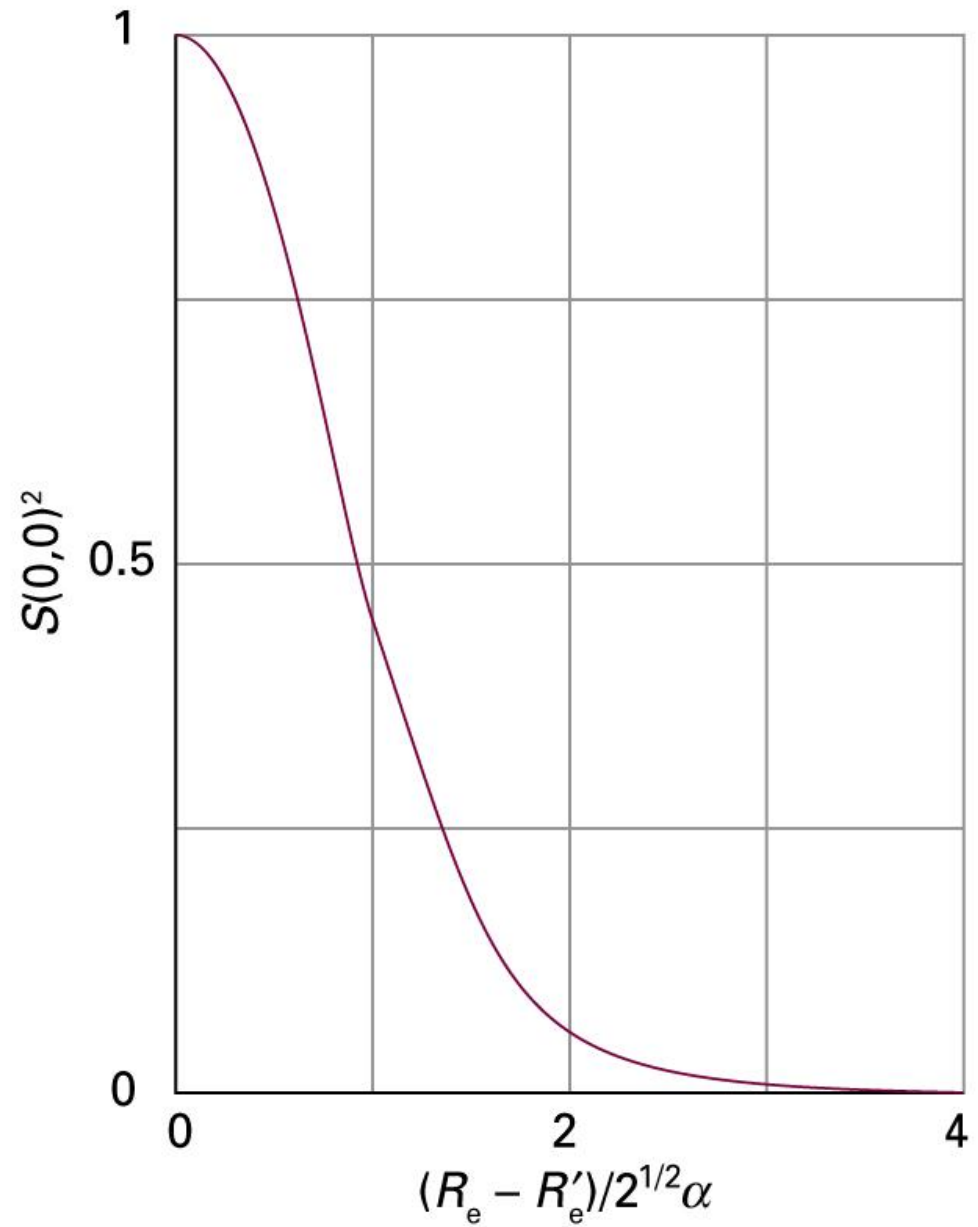
$$\mu = -e \sum_i r_i + e \sum_I Z_I R_I$$

Intensity=
   square modulus of dipole moment
   +overlap integral $S(v_f, v_i)$

(S=1 perfect match, S=0 no overlap)

•Frank-Condon factor: $|S|^2$

- The Franck-Condon factor for the arrangement discussed in Example 13.1

- The model wavefunctions used in Self-test 13.2
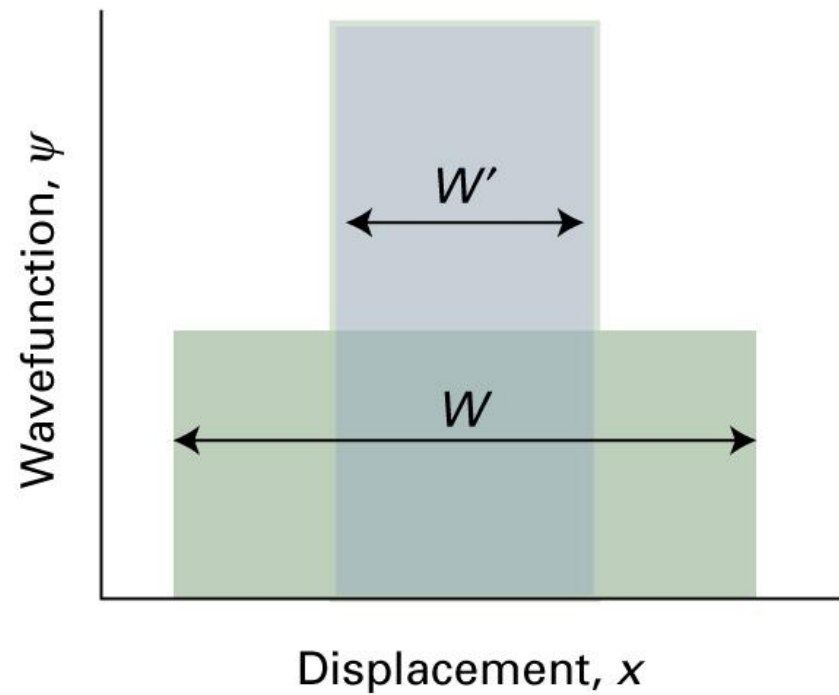
Rotational structure

• rotational transition accompany the vibrational excitation that accompanies electronic excitation

$$E(J) = hcBJ(J+1) \qquad E(J') = hcB'J'(J'+1)$$

Branch as in vibrational spectroscopy,

P branch $(\Delta J = -1)$: $\tilde{\nu}_P(J) = \tilde{\nu} - (B'+B)J + (B'-B)J^2$

Q branch $(\Delta J = 0)$: $\tilde{\nu}_Q(J) = \tilde{\nu} + (B'-B)J(J+1)$

R branch $(\Delta J = +1)$: $\tilde{\nu}_R(J) = \tilde{\nu} + (B'+B)(J+1) + (B'-B)(J+1)^2$

• Difference:
electronic excitation results in much larger changes in bond length than vibrational excitation causes alone

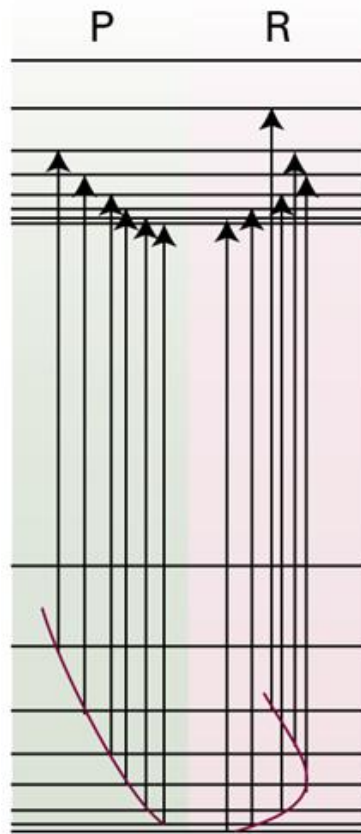# Band head

When the rotational constants of a diatomic molecule differ significantly,

bond length
excited state>gnd state
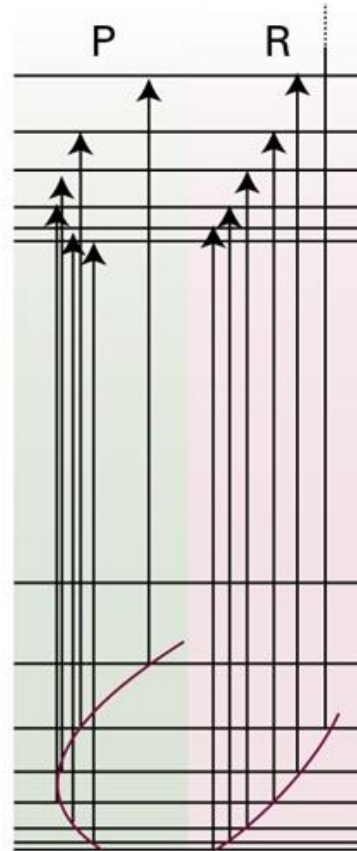$B'<B$

bond length
excited state<gnd state
$B'>B$

(a) $\tilde{B}' < \tilde{B}$

(b) $\tilde{B}' > \tilde{B}$

a head in the R branch
when $B'<B$

a head in the P branch
when $B'>B$

13.3 The electronic spectra of polyatomic molecules

chromophores: groups with characteristic optical absorptions

-d-d transitions
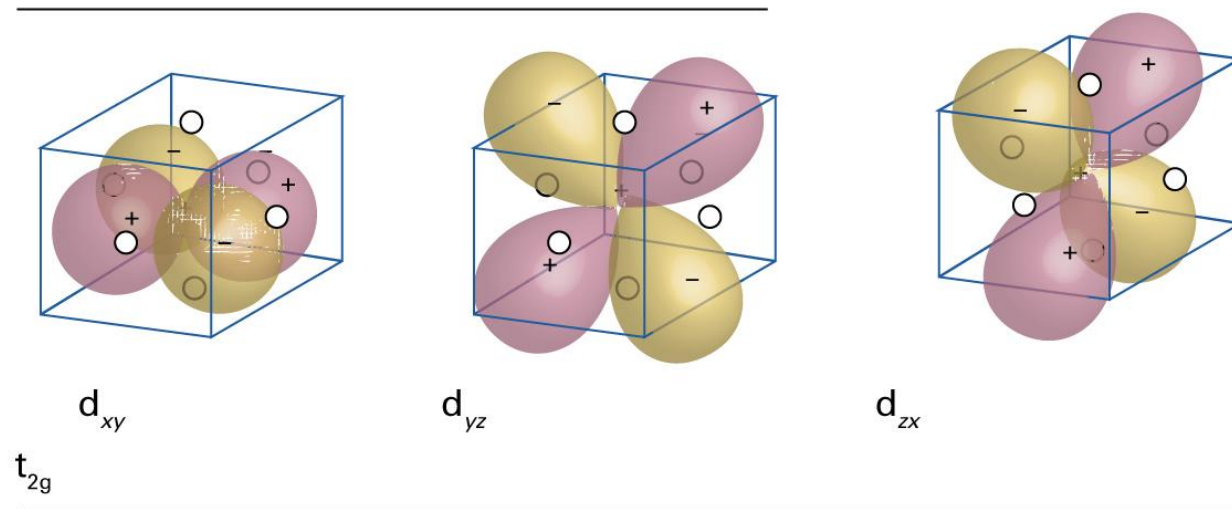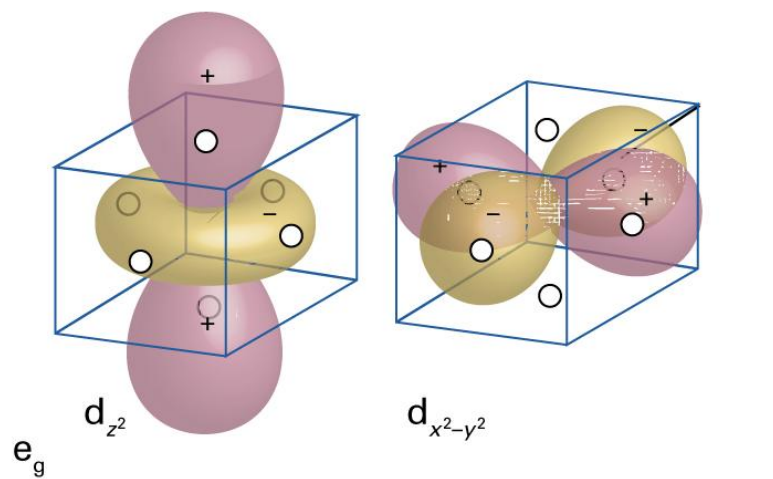
-charge transfer transitions

-$\pi^* \leftarrow \pi$ and $\pi^* \leftarrow n$ transitions

Table 13.2* Absorption characteristics of some groups and molecules

Group	$\tilde{v}/\text{cm}^{-1}$	λ_{max}/nm	$\varepsilon/(\text{dm}^3\,\text{mol}^{-1}\,\text{cm}^{-1})$
C=C ($\pi^\star \leftarrow \pi$)	61 000	163	15 000
	57 300	174	5 500
C=O ($\pi^\star \leftarrow$ n)	35 000–37 000	270–290	10–20
H_2O ($\pi^\star \leftarrow$ n)	60 000	167	7 000

* More values are given in the *Data section.*

d_{z^2} $d_{x^2-y^2}$

e_g

d_{xy} d_{yz} d_{zx}

t_{2g}

-d-d transitions

in free atom, all d orbitals are degenerate
in d-metal complex, e- absorbs E and makes transitions
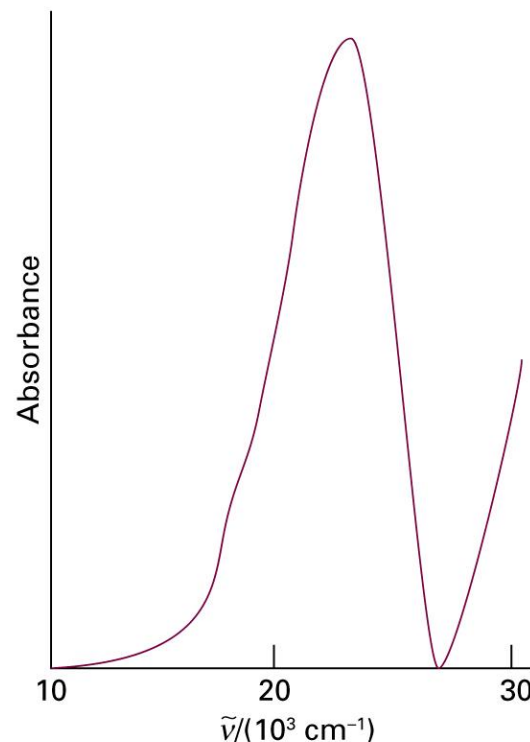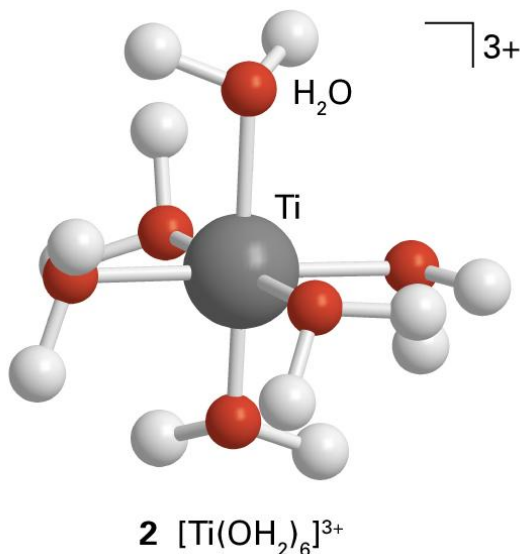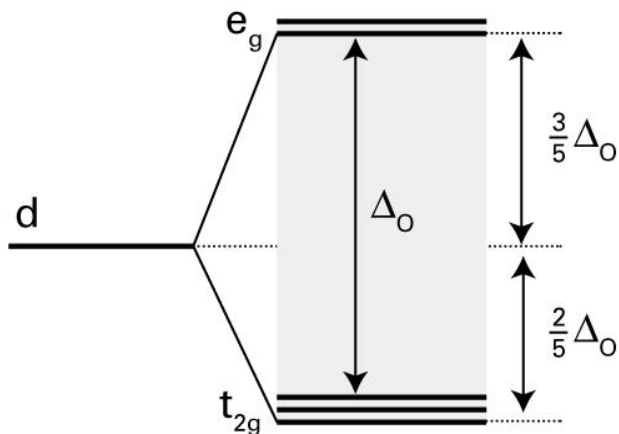
ex. The electronic absorption spectrum of $[Ti(OH_2)_6]^{3+}$ in aqueous solution

-according to Laporte rule:
d-d transitions are parity forbidden in octahedral complexes (g->g transition)

BUT, d-d transitions are vibronically allowed by asymmetrical vibration (weak)

-charge transfer transitions

• transfer an e-
  from the ligand to central atom

-transition dipole moment is large -> strong intensity
(e- moves considerable distance)

-but, little overlap of initial and final wavefunctions for large
separations can lead to low intensity

ex. MnO_4^-: 420 ~ 700 nm
e- migration LMCT (ligand-to-metal charge-transfer)
e- migration MLCT (metal-to-ligand charge-transfer)

# $\pi^* \leftarrow \pi$ and $\pi^* \leftarrow n$ transitions

-absorption by a C=C double bond: 7eV

-when the double bond is part of a conjugated chain,
   the energies of the molecular orbitals: closer together
   $\pi^* \leftarrow \pi$ transition longer wavelength
   (even in visible region)

(box 17.1)

• C=C double bond as a chromophore

important transitions is the $\pi^* \leftarrow \pi$
transition:
an electron is promoted from a п orbital
to the corresponding antibonding orbital

π^*

π
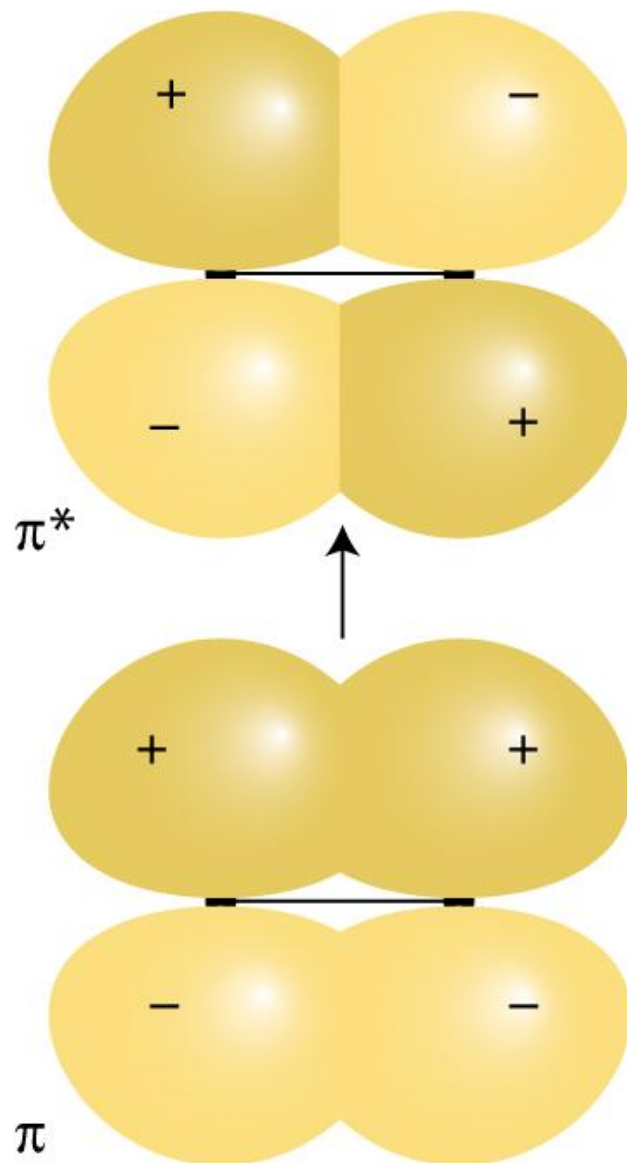
- Carbonyl group (C=O) as a chromophore

primarily on account of the excitation
of a nonbonding O lone-pair electron
to an antibonding CO π orbital
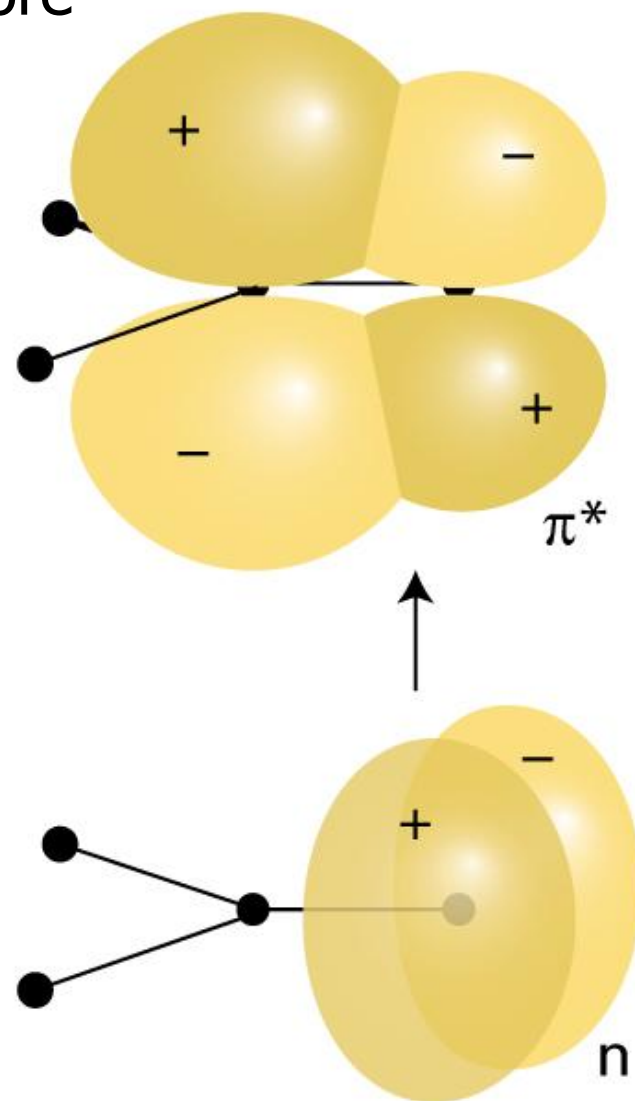
typically 4 eV, 290 nm
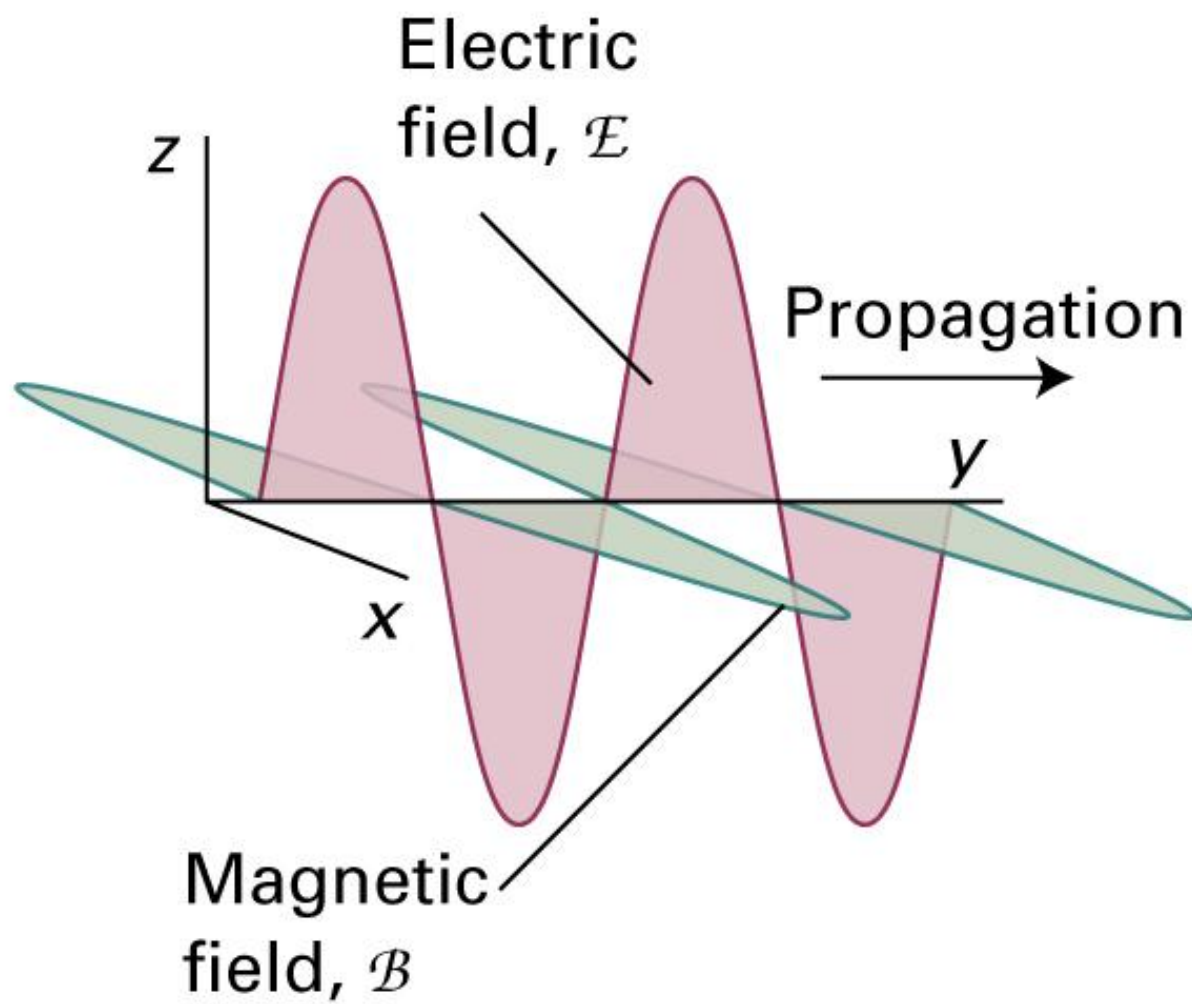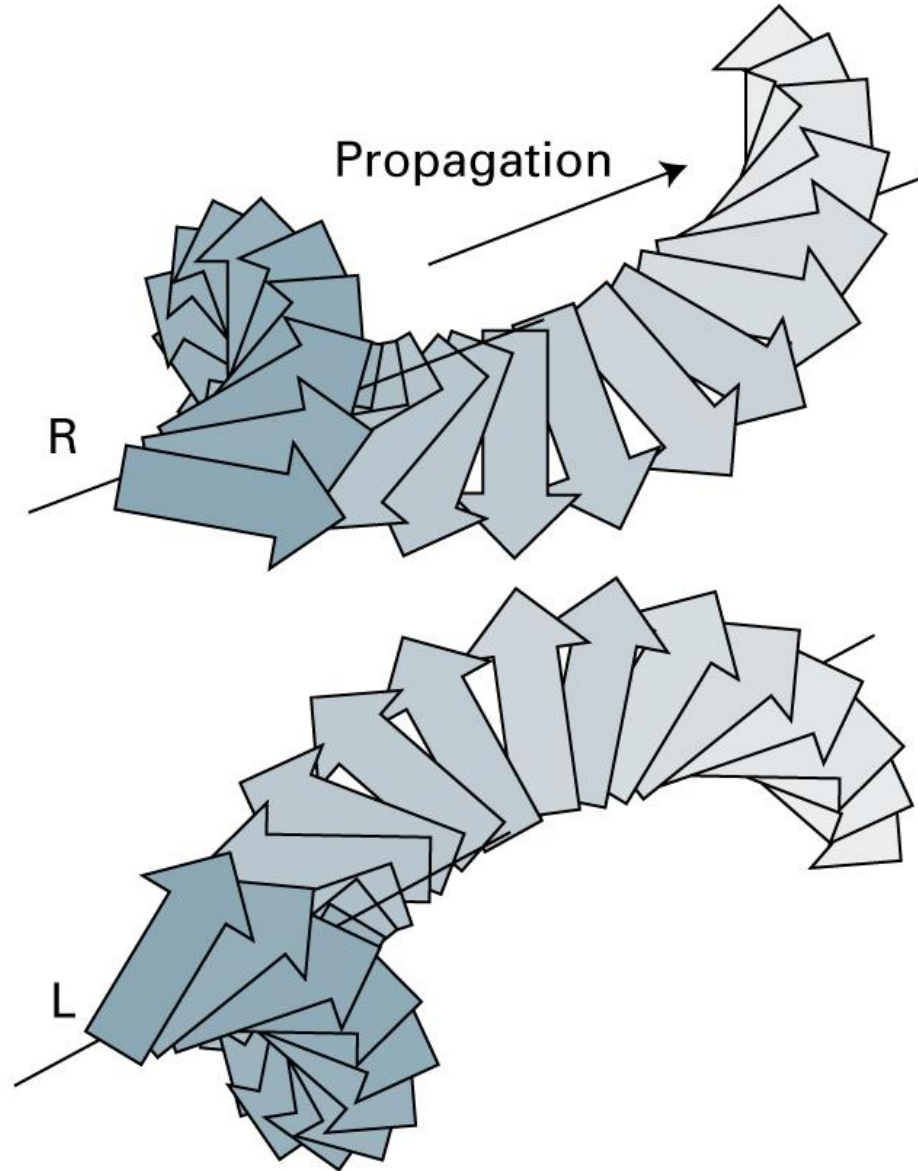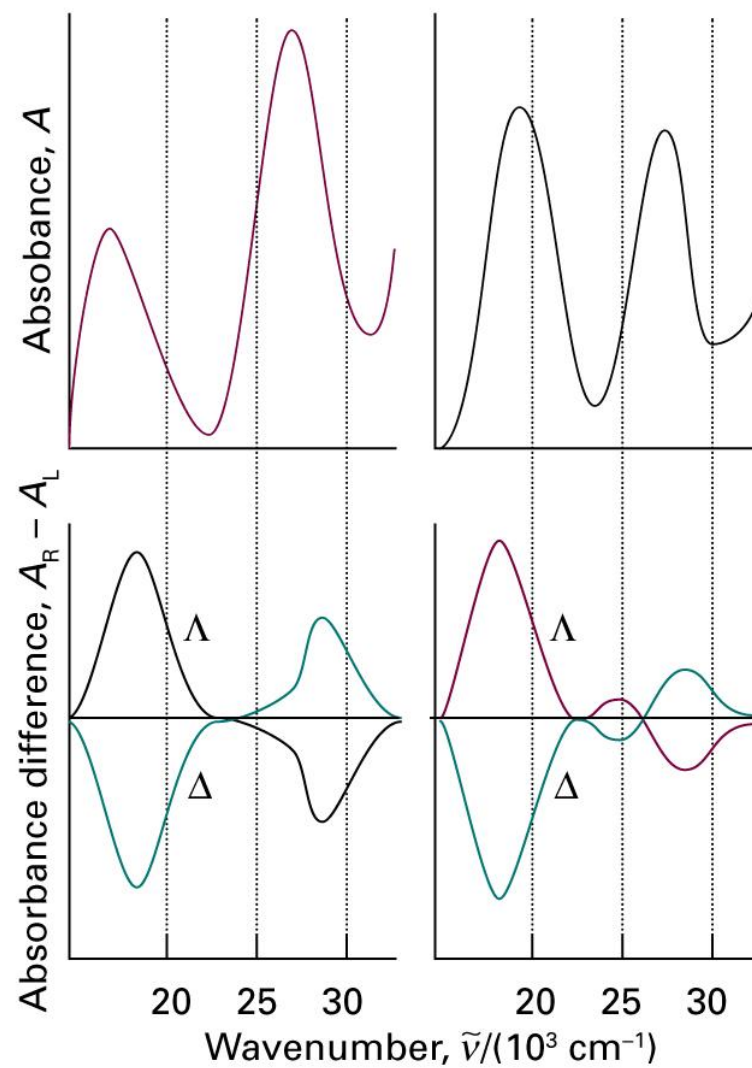symmetry forbidden: weak absorption

Figure 13.16

Electric field, $\mathcal{E}$

Propagation

Magnetic field, $\mathcal{B}$

Figure 13.17

Propagation

R

L
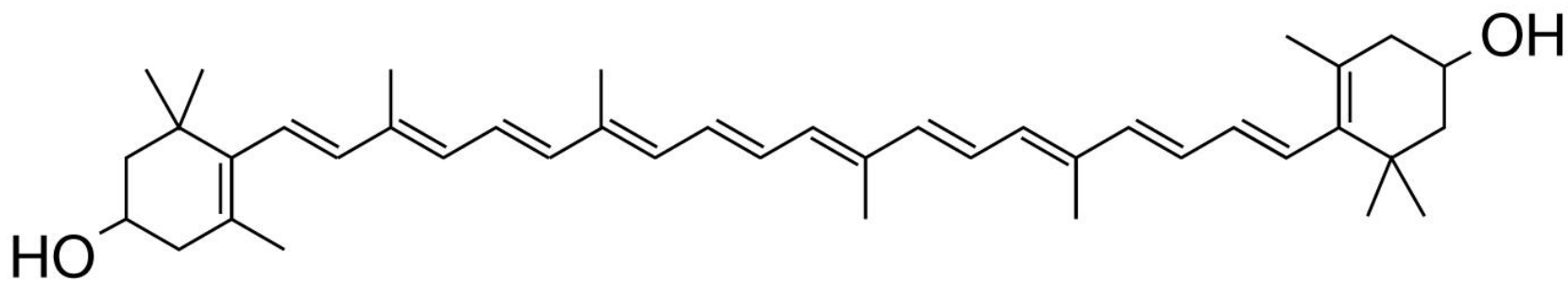
Figure 13.18

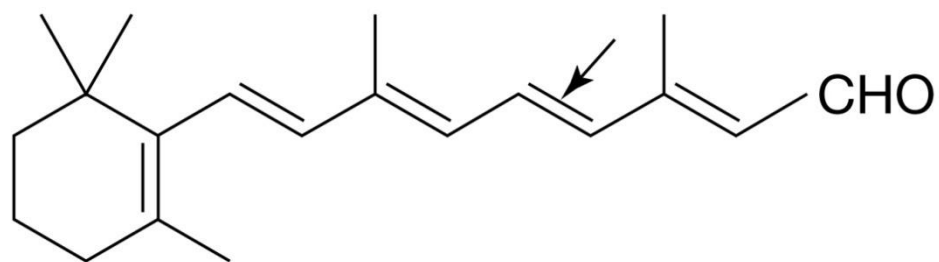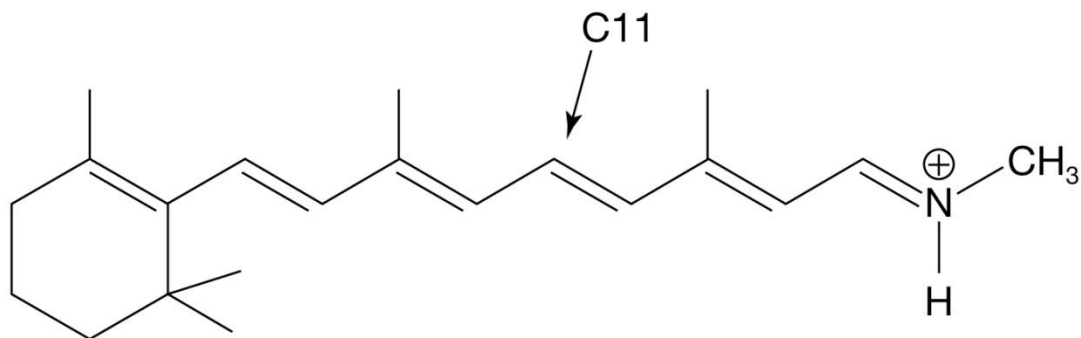**2** A xanthophyll
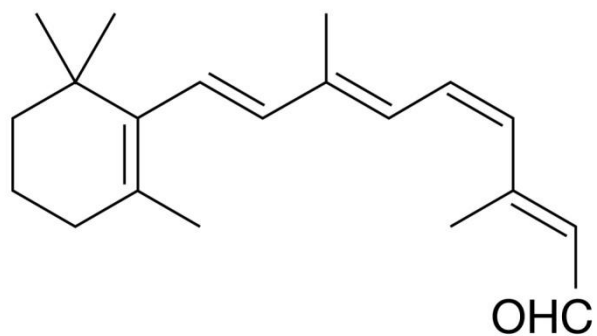
3 11-*cis*-retinal

4 All-*trans*-retinal

C11

5
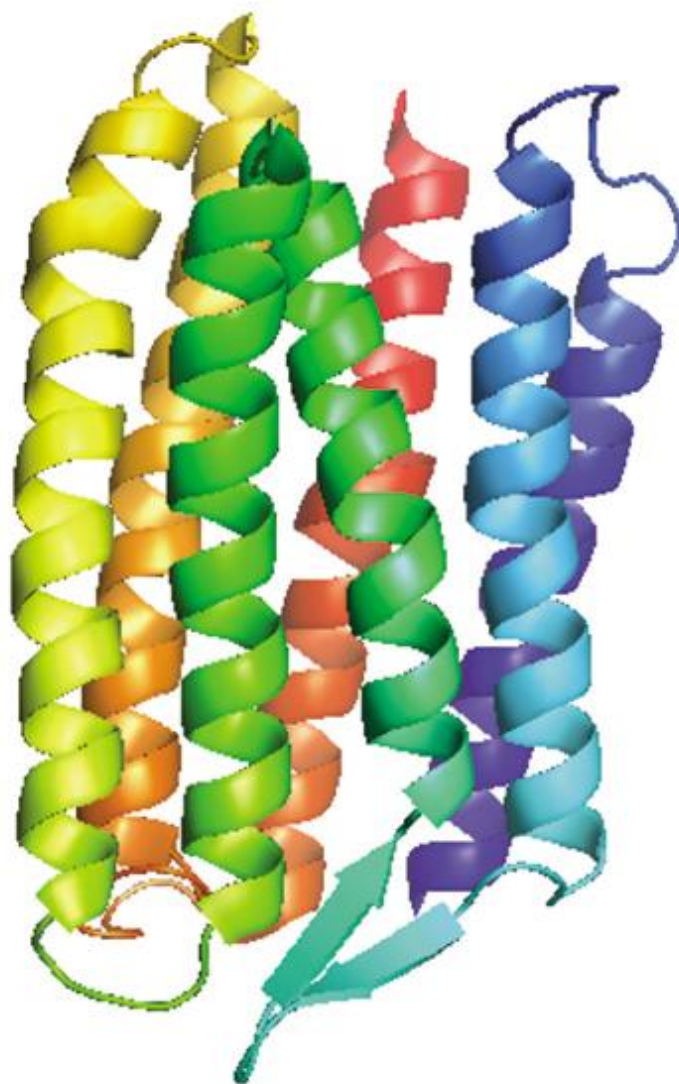
Figure 13.19

The fates of electronically excited states

## 13.4 Fluorescence and phosphorescence

13.5 Dissociation and predissociation

13.6 Laser

- radiative decay process:
  a process in which a molecule discards its excitation E as **photon**

- nonradiative decay process:
  the excess E is transferred into vib, rot, and translation
  of the surrounding molecules

13.4 Fluorescence and phosphorescence

- The empirical (observation-based) distinction

- fluorescence ~ extinguished very quickly after the removal ofexciting source

- Phosphorescence ~ relatively slowly diminishing intensity.
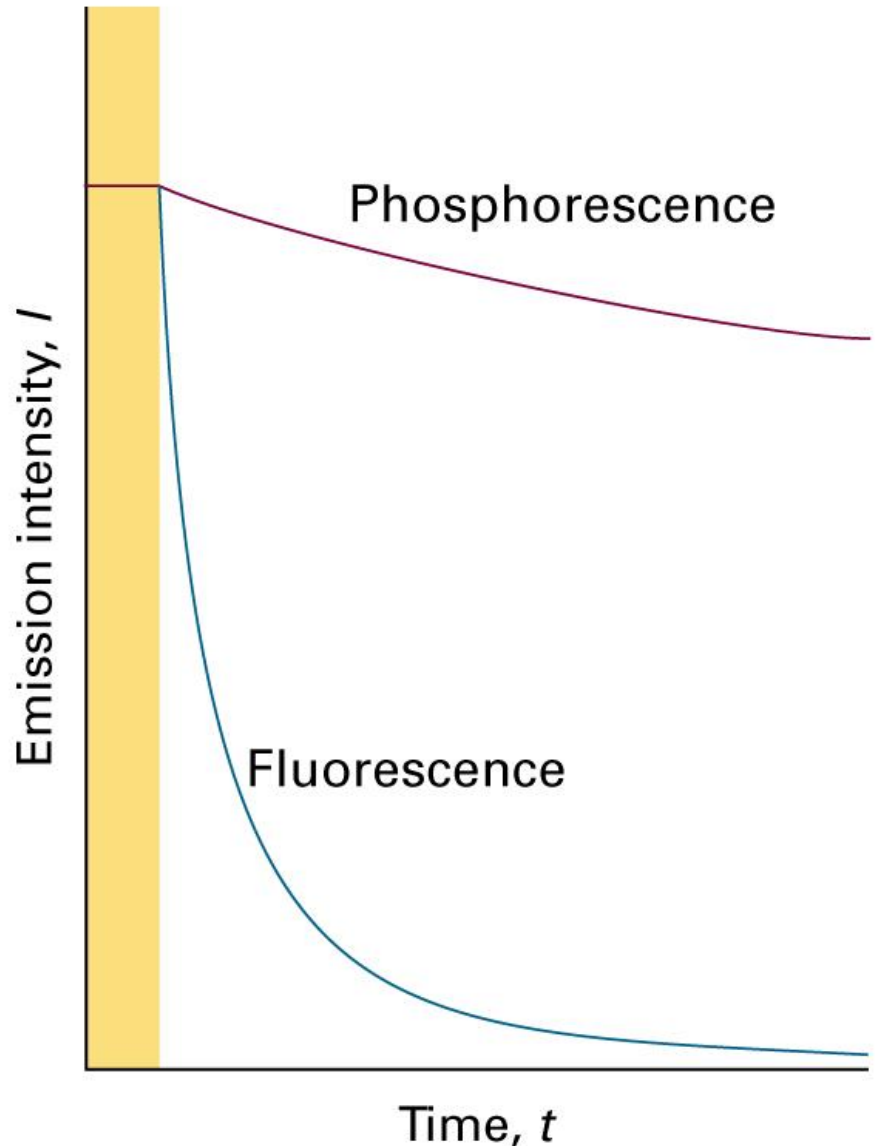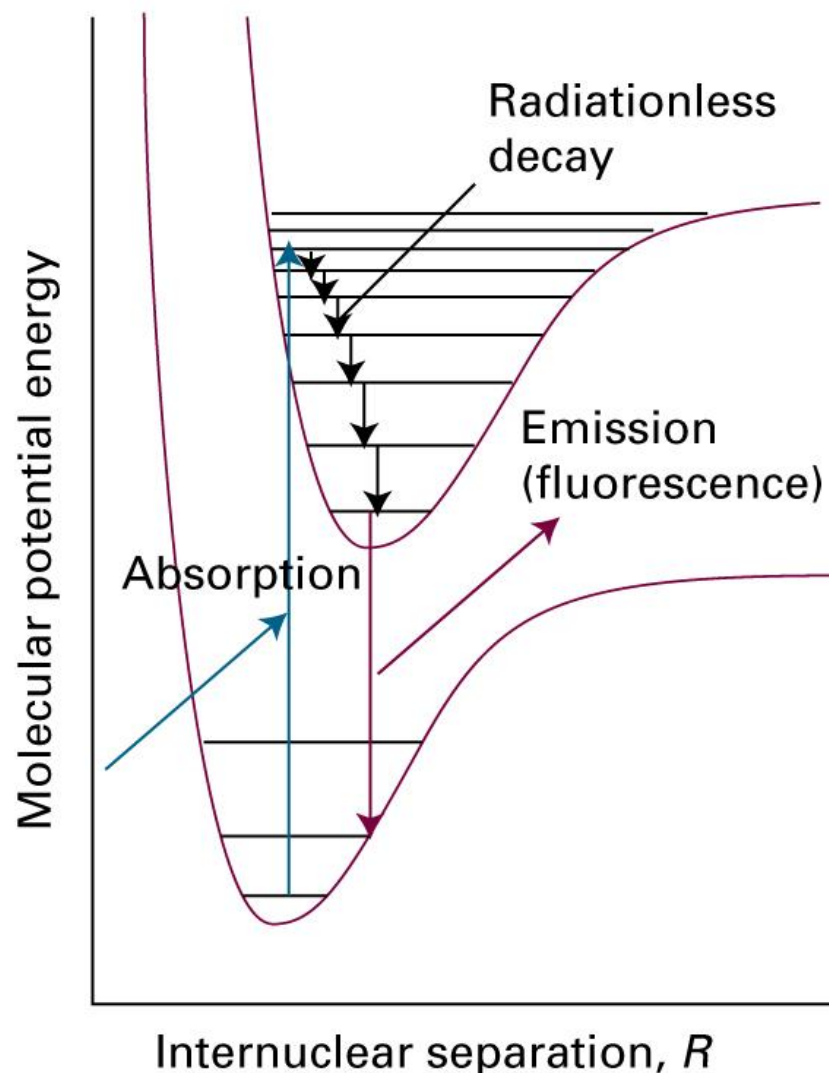
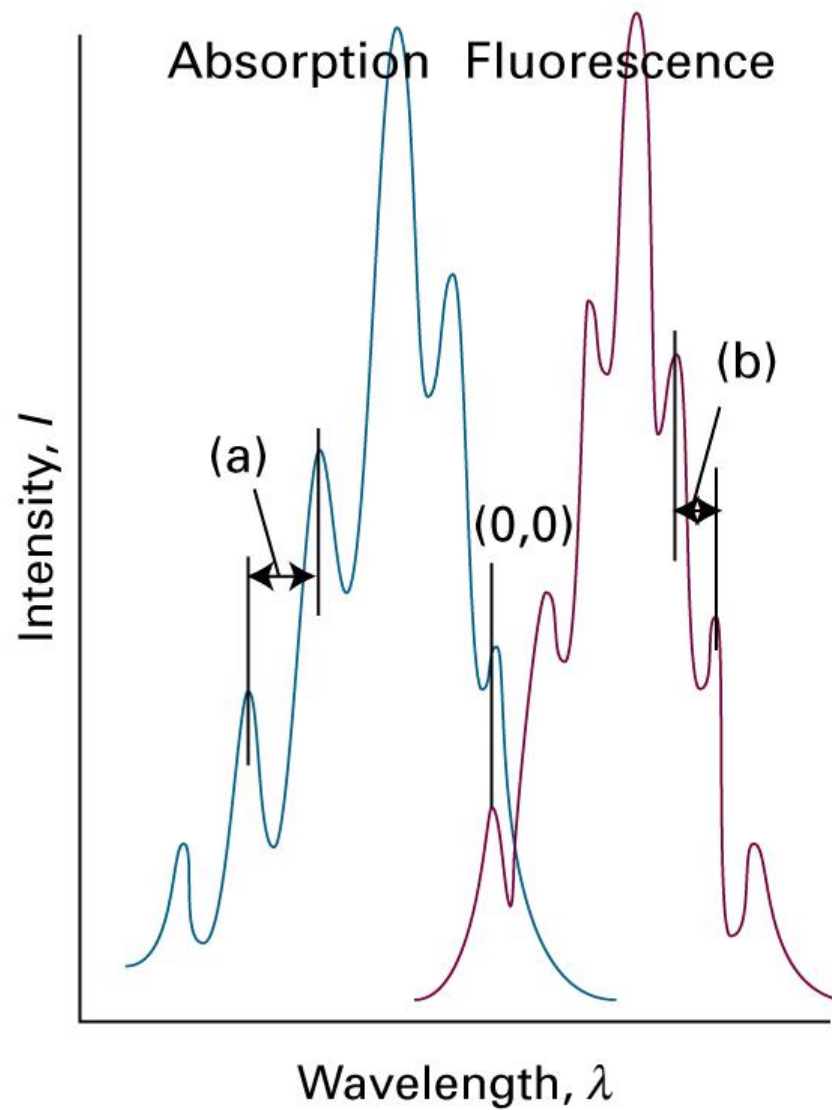# -fluorescence

initial absorption

radiationless decay
in the upper vibrational states by giving
up energy to the surroundings

A radiative transition

from the vibrational ground state
of the upper electronic state.

-note:
•the 0-0 transitions are coincident
•a mirror image

the shift of the fluorescence spectrum relative to the absorption spectrum due to solvent
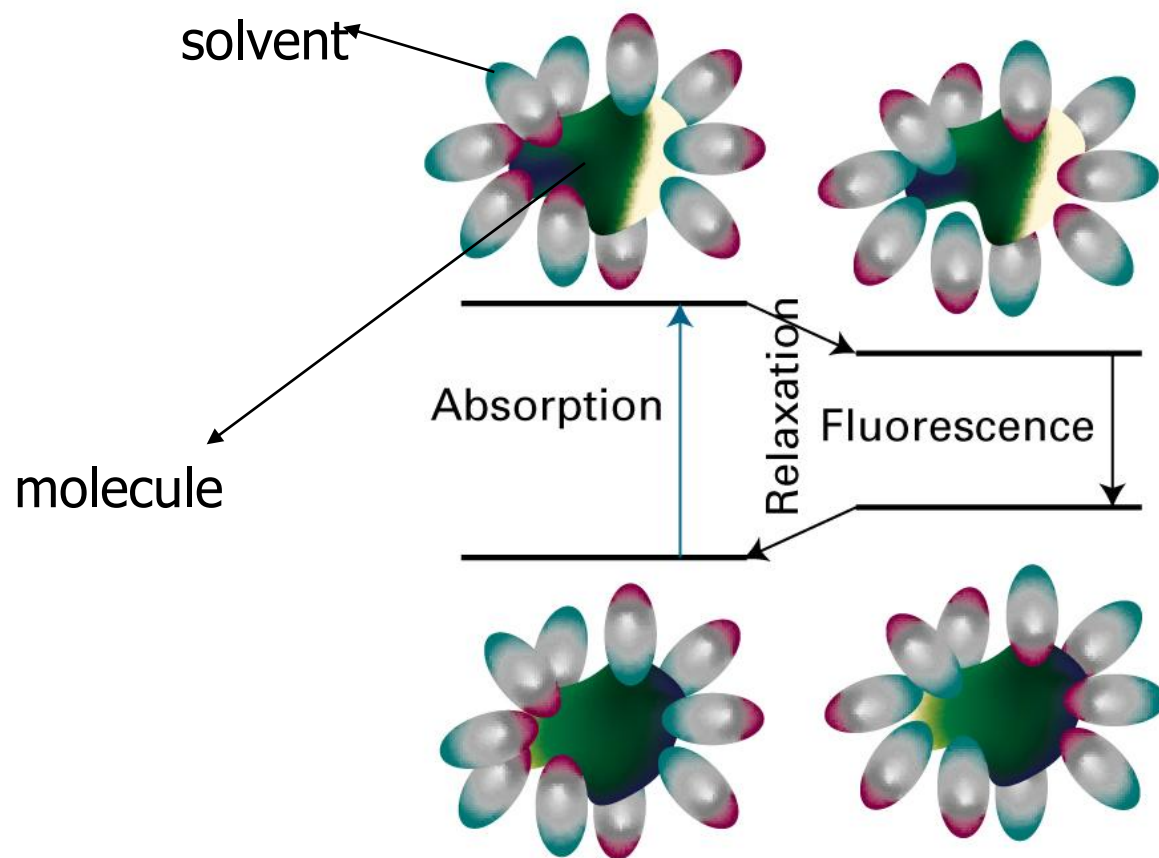
- the absorption occurs with the solvent in the arrangement characteristic of the ground electronic state of the molecules

- before fluorescence occurs, the solvent molecules relax into a new arrangement, and that arrangement is preserved during the subsequent radiative transition.

•phosphorescence

•**intersystem crossing**:

-the important step in phosphorescence

-the switch from a **singlet** state to a **triplet** state by **spin-orbit coupling**

-the triplet state acts as a slowly radiating reservoir because the return to the ground state is **spin-forbidden**

Phosphorescence should be the most intense from **solid samples**: less efficient E transfer, ISC has time to occur
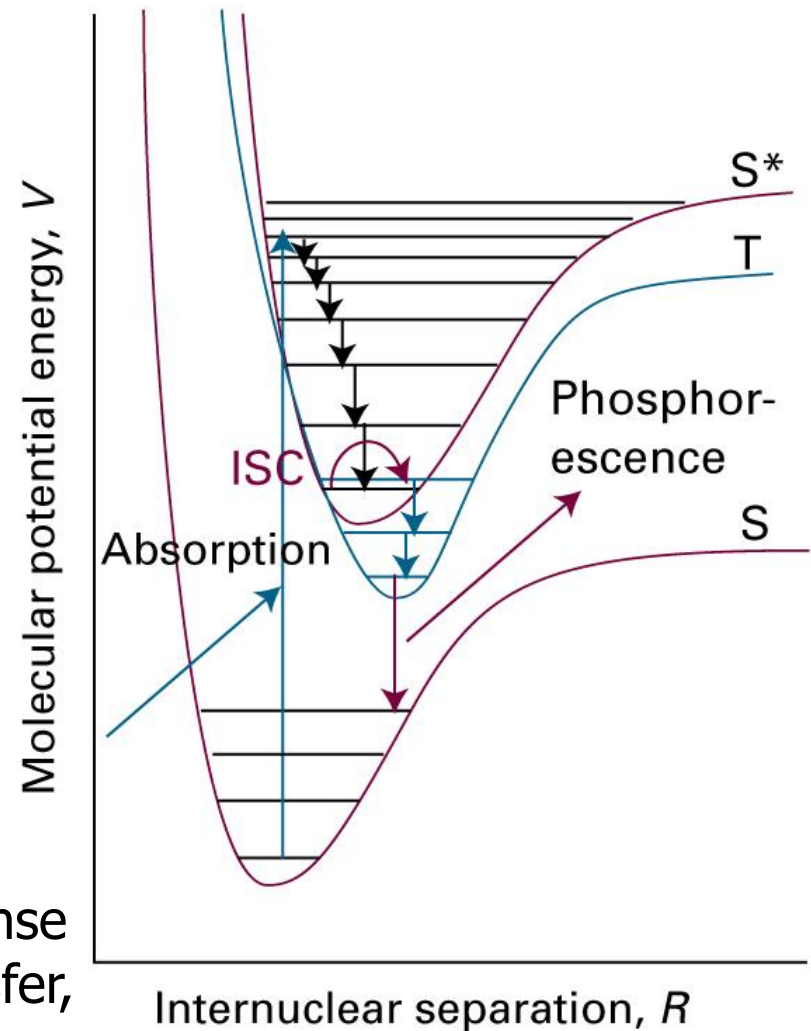
•A Jablonski diagram

ex) naphthalene

-a simplified portrayal of the relative positions of the electronic energy levels of a molecule

-The ground vibrational state of each electronic state are correctly located vertically but the other vibrational states are shown only schematically.

(**IC:internal conversion;
ISC:intersystem crossing**)
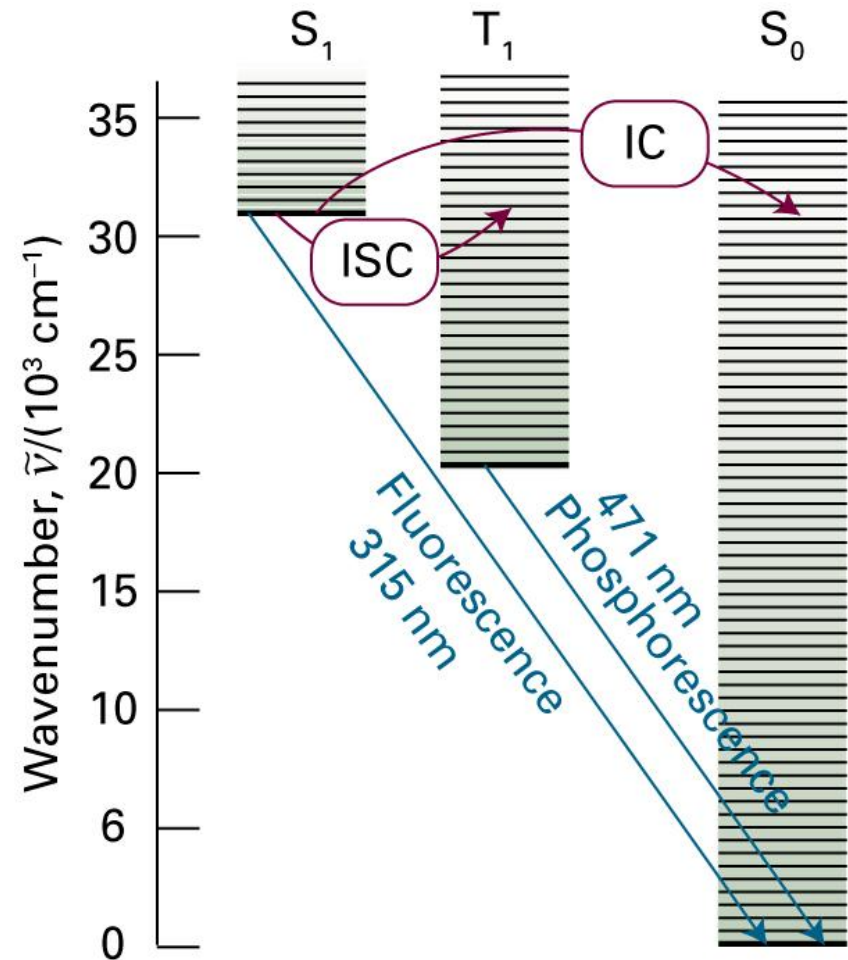
13.5 Dissociation and predissociation

-Dissociation

•When absorption occurs to unbound states of the upper electronic,
the molecule dissociates and the absorption is a continuum.

•Below the dissociation limit,
the electronic spectrum shows a normal vibrational structure.
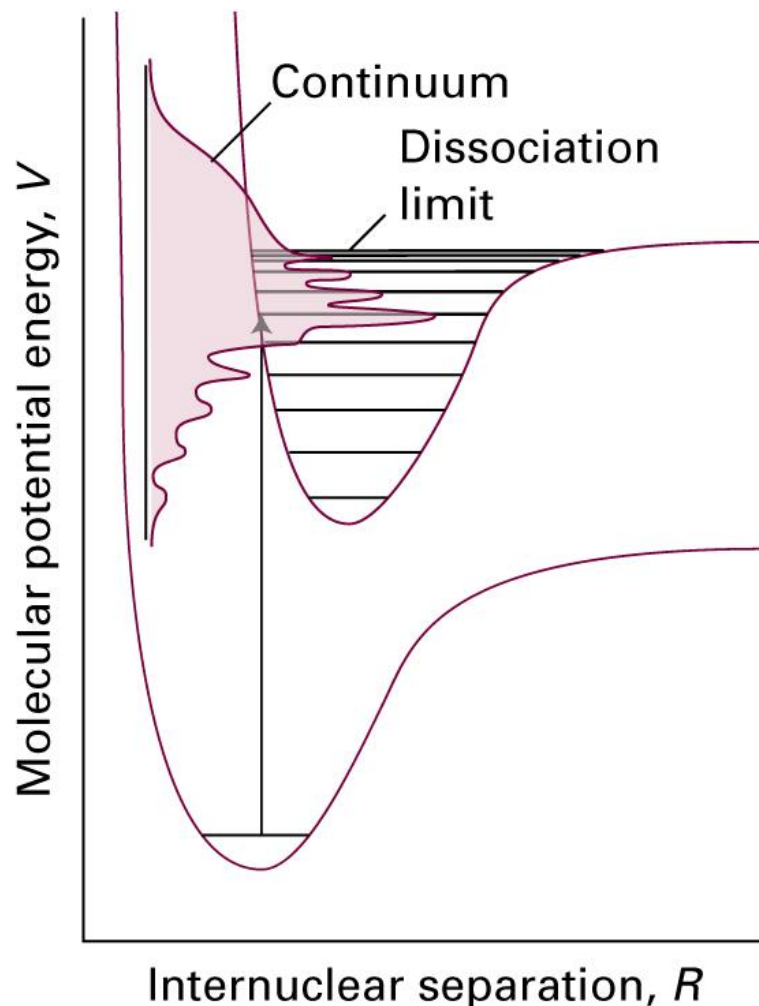
-predissociation

•When a dissociative state crosses a bound state, molecules excited to levels near the crossing may dissociate.

•Predissociation is detected in the spectrum as a loss of vibrational structure that resumes at higher frequencies.
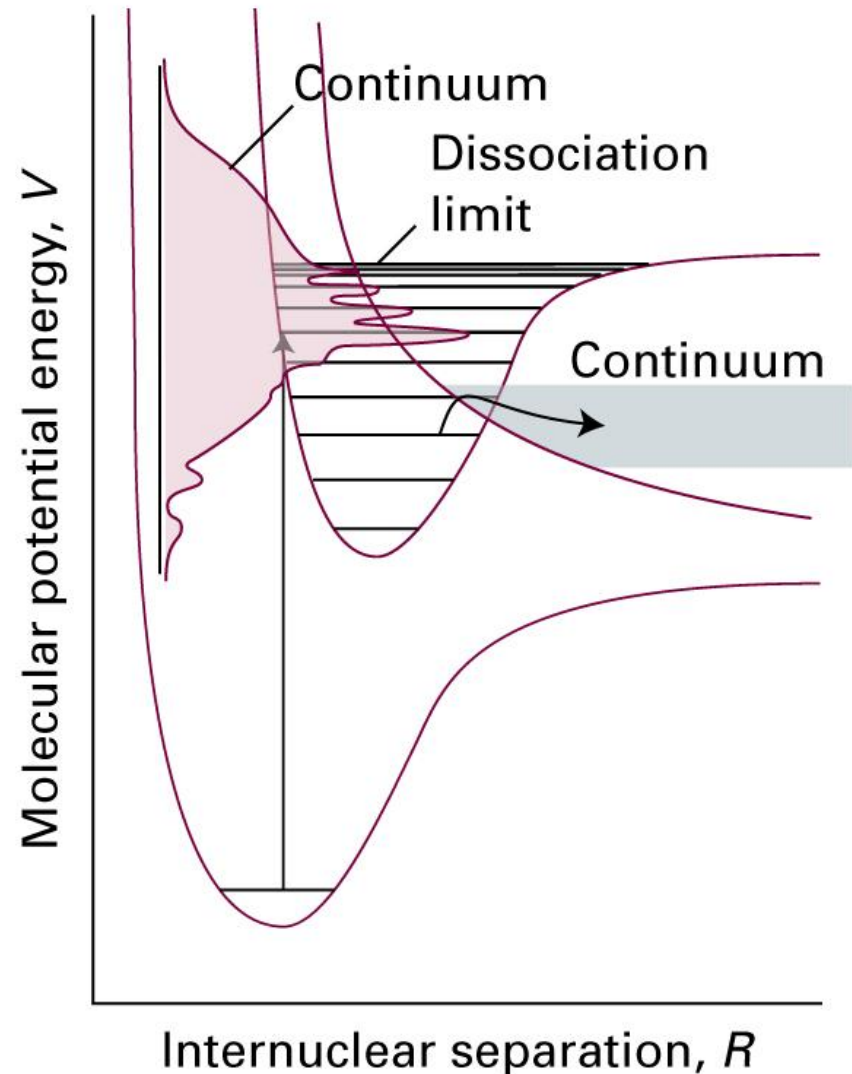
13.6 Laser action

laser: **l**ight **a**mplification by **s**timulated **e**mission of **r**adiation

requirement:

1. metastable excited state
(an excited state with a long enough life time to participate in stimulated emission)

2. the existence of a greater population in the metastable state than in the lower state

Table 13.3 Characteristics of laser radiation and their chemical applications

Characteristic	Advantage	Application
High power	Multiphoton process Low detector noise High scattering intensity	Spectroscopy Improved sensitivity Raman spectroscopy (Chapter 12)
Monochromatic	High resolution State selection	Spectroscopy Photochemical studies (Chapter 21) State-to-state reaction dynamics (Chapter 22)
Collimated beam	Long path lengths Forward-scattering observable	Improved sensitivity Raman spectroscopy (Chapter 12)
Coherent	Interference between separate beams	CARS (Chapter 12)
Pulsed	Precise timing of excitation	Fast reactions (Chapters 21 and 22) Relaxation (Chapter 21) Energy transfer (Chapter 21)

Spontaneous emission

An atom in the excited state will spontaneously decay:

decay rate ~ N_2 (the number of atoms in the excited state)

The photons are emitted
- **stochastically** (randomly)
- **incoherently** (no fixed phase relationship among photons emitted from a group of excited atoms)

the number of atoms in the excited state at time t:

$$N_2(t) = N_2(0) \exp(-t / T_{21}),$$

where $N_2(0)$ is the number of excited atoms at time $t=0$, and T_{21} is the *lifetime* of the transition between the two states.

•Boltzmann distribution
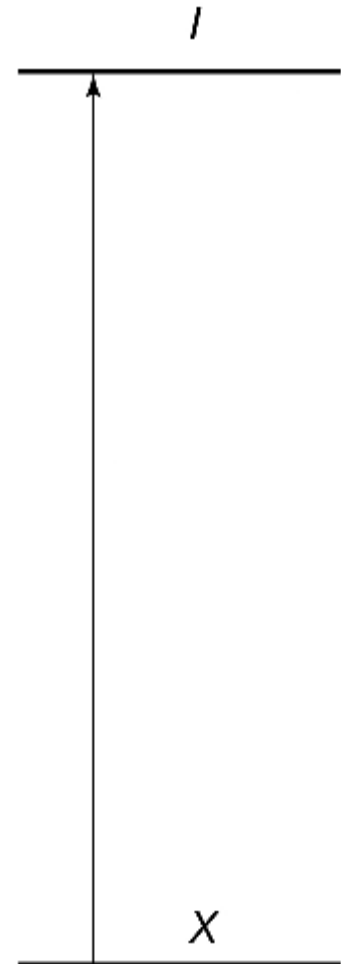
at thermal equilibrium,
Boltzmann distribution

$$N_2/N_1 = \exp[-(E_2-E_1)/kT]$$

at thermal equilibrium,
$N_2 < N_1$ all the time

at best,

$$N_2/N_1 \sim 1$$

2: excited
state

I

1: ground
state

x

Stimulated emission

An atom in the excited state will spontaneously decay:

decay rate ~ N_2 (the number of atoms in the excited state)
plus radiation density of light

The photons are emitted
-**coherently** (the same phase among photons emitted from a
group of excited atoms)

the number of atoms in the excited state at time t:

$N_2(t) = N_2(0) \exp(-t / T_{21})$,

where $N_2(0)$ is the number of excited atoms at time $t=0$, and T_{21} is
the *lifetime* of the transition between the two states.

•steps leading to laser action

(a) The Boltzmann population of states, with more atoms in the ground state.

(b) When the initial state absorbs, the populations are inverted (the atoms are pumped to the excited state).
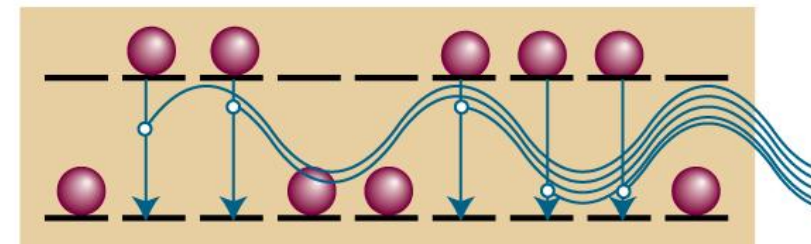
(c) A cascade of radiation then occurs, as one emitted photon stimulates another atom to emit, and so on. The radiation is coherent (phase in step).
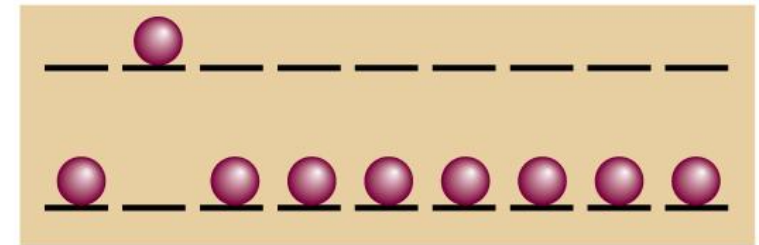
(a) Thermal equilibrium
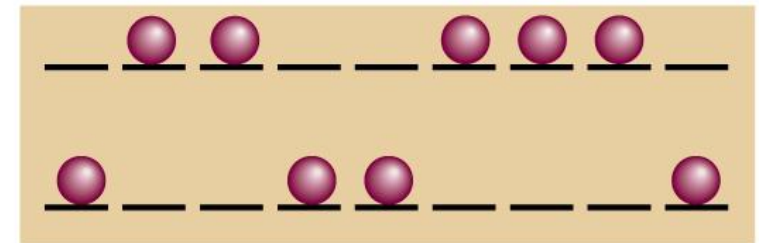
Pump

(b) Population inversion

(c) Laser action

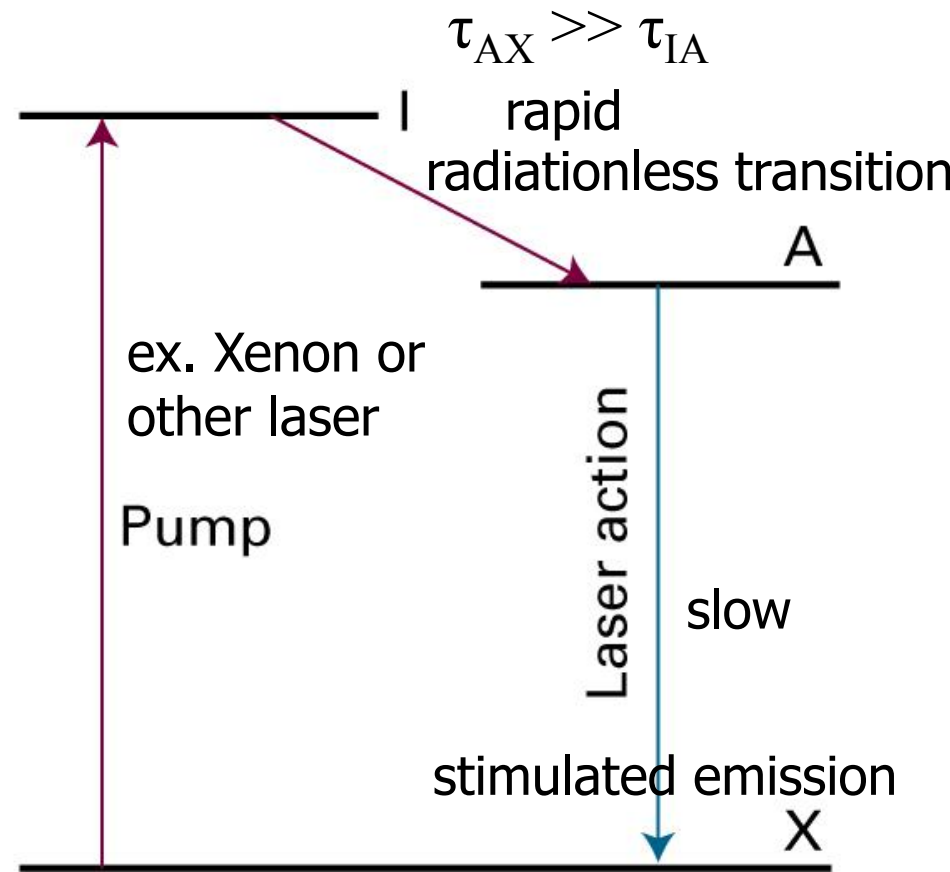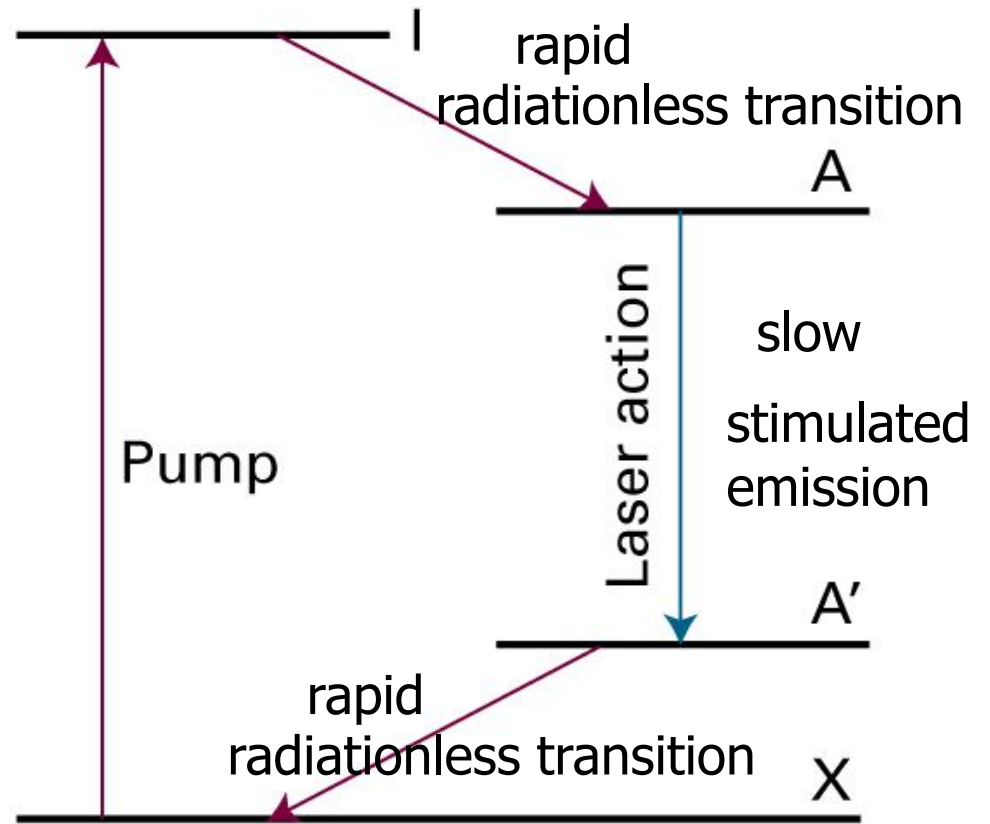# •Population inversion

-three level laser

initially, $N_X \sim N$, $N_I \sim 0$

due to the radiationless transition, $N_X < N_A$

The pumping pulse populates the intermediate state I, which in turn populates the laser state A. The laser transition is the A → X

$$\tau_{AX} \gg \tau_{IA}$$

I   rapid
radiationless transition

A

ex. Xenon or other laser

Pump

Laser action

slow

stimulated emission
X

-four level laser

I

rapid
radiationless transition

A

Pump

Laser action

slow

stimulated
emission

A'

rapid
radiationless transition

X

Because the laser transition
terminates in an excited state (A'),
the population inversion between A
and A' is much easier to achieve.

•Cavity and mode characteristics [1]

•Cavity (or cavity mode):
between two mirrors, reflecting the light back and forth

$$n \times \frac{1}{2}\lambda = L \quad \text{otherwise destructive}$$

•resonant mode of cavity (or resonant cavity):

-not all wavelength (that can be sustained by the cavity) are amplified by the laser

-differ in frequency by multiples of c/2L

-only photons that are traveling strictly parallel to the axis of cavity undergo more than a couple of reflections. -> only they are amplified

-> laser light form a beam of very low divergence

•Cavity and mode characteristics [2]

Laser radiation: coherent (all EM waves are in step)

spatial coherence: the waves are in step across the cross-section
of the beam emerging from the cavity

temporal coherence: the waves in step along the beam

coherence length: the distance over which the waves
remain coherent

$$l_c = \frac{\lambda^2}{2\Delta\lambda}$$

light bulb: $l_c \sim 400$ nm coherence length
He-Ne laser with $\Delta\lambda \sim 2$pm: $l_c \sim 10$ cm coherence length

•Q-switching

-an artificial technique to obtain an intense short pulse (~5ns duration)
-detour overheating problem
-the modification of the resonance characteristics of the laser cavity

-If a laser is operated continuously, output of the laser will be constant for steady operation -> overheating

-If the laser action is prevented temporarily and allow a build up of population inversion,
a high density of excited species will be obtained.

-When these species are let to lase almost simultaneously, we can obtain a strong pulse.

The principle of Q-switching

(a) The excited state is populated while the cavity is non-resonant.
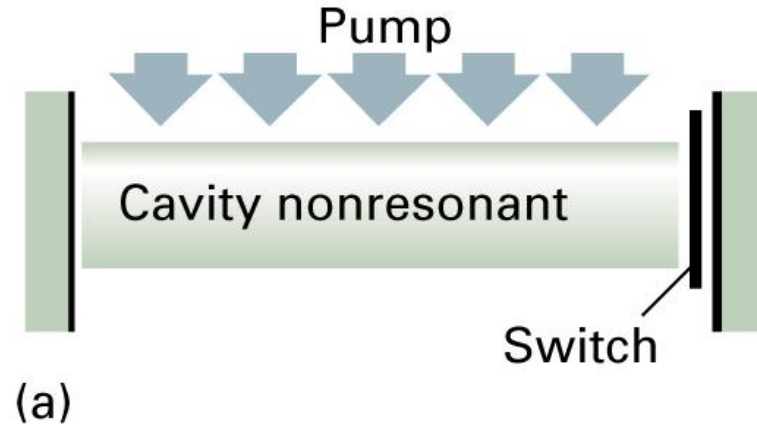
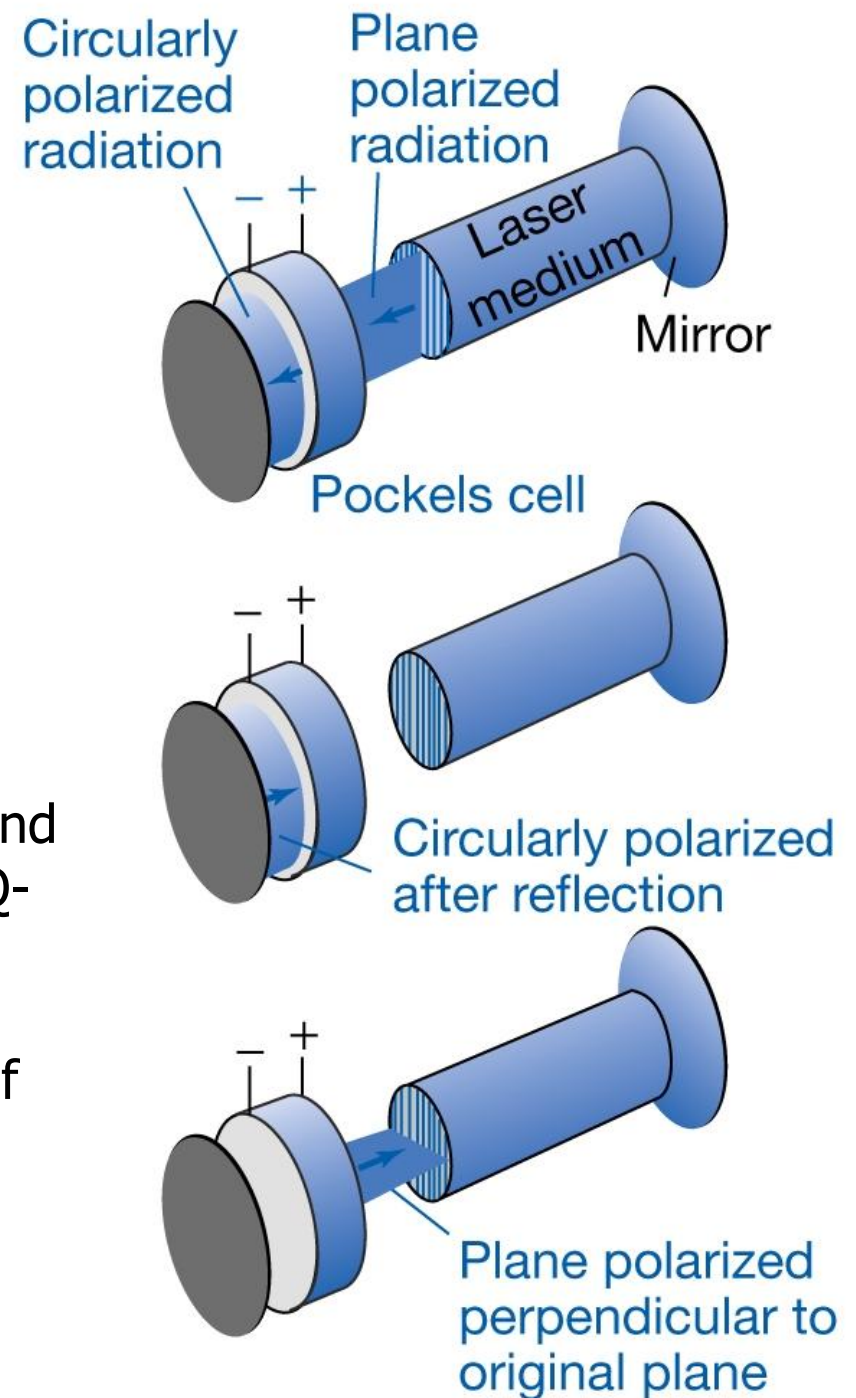(b) Then the resonance characteristics are suddenly restored, and the stimulated emission emerges in a giant pulse.

Pump

Cavity nonresonant

Switch

(a)

Cavity resonant

Pulse

(b)
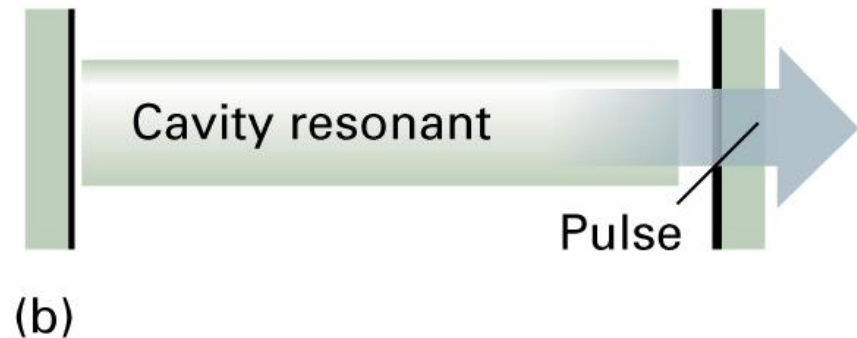
•One way of Q-switching

-Pockels cell

(electro-optical device converting from plane-polarized light to circularly-polarized light)

When light passes through a cell that is 'on', its plane of polarization is rotated and so the laser cavity is non-resonant (its Q-factor is reduced).

When the cell is turned off, no change of polarization occurs, and the cavity becomes resonant.

Circularly polarized radiation

Plane polarized radiation

Laser medium

Mirror

Pockels cell

Circularly polarized after reflection

Plane polarized perpendicular to original plane

•Another way of Q-switching

-Saturable absorber

ex. dye that loses its mobility to absorb when many of its molecules have been excited by intense radiation. (Suddenly the dye becomes transparent.)

• Mode locking

-technique producing intense pulses of picosecond duration or less

-radiation from cavity mode and resonance mode have random phases

    ↓ mode-lock phases

-sharp peaks

-varying the Q-switching of the cavity periodically at the freq c/2L...
(opening of shutter in synchrony with the round trip travel time of the photon in the cavity)

-this modulation could be achieved by **linking a prism (the cavity) to a transducer** driven by a radiofrequency source at a frequency 'c/2L'

1 ns   1 ps

Time, *t* ⟶
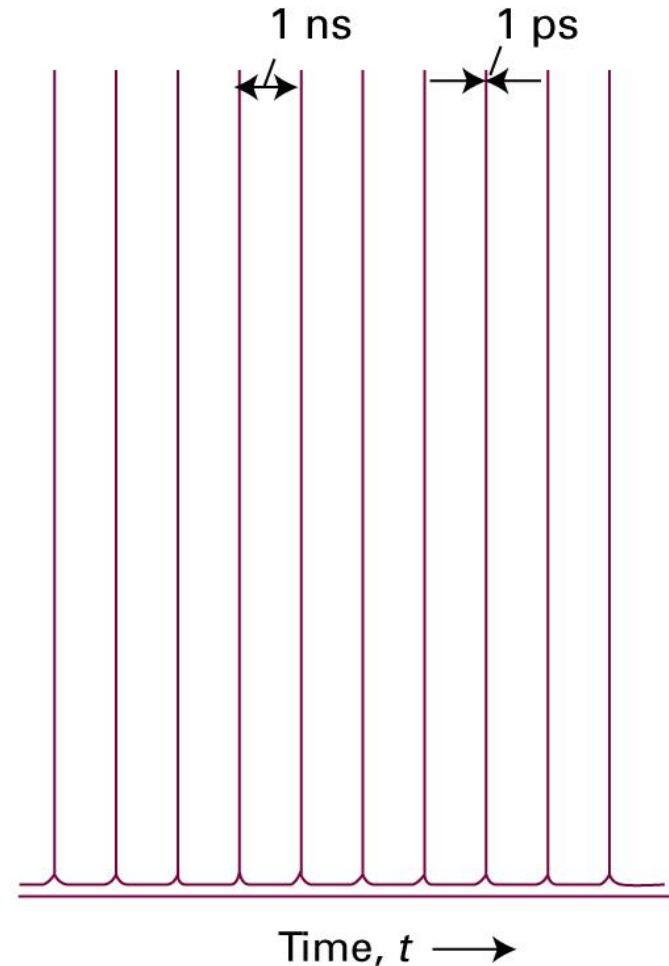
a mode-locked laser:
a stream of narrow pulses by an interval for a photon to make **a round trip**

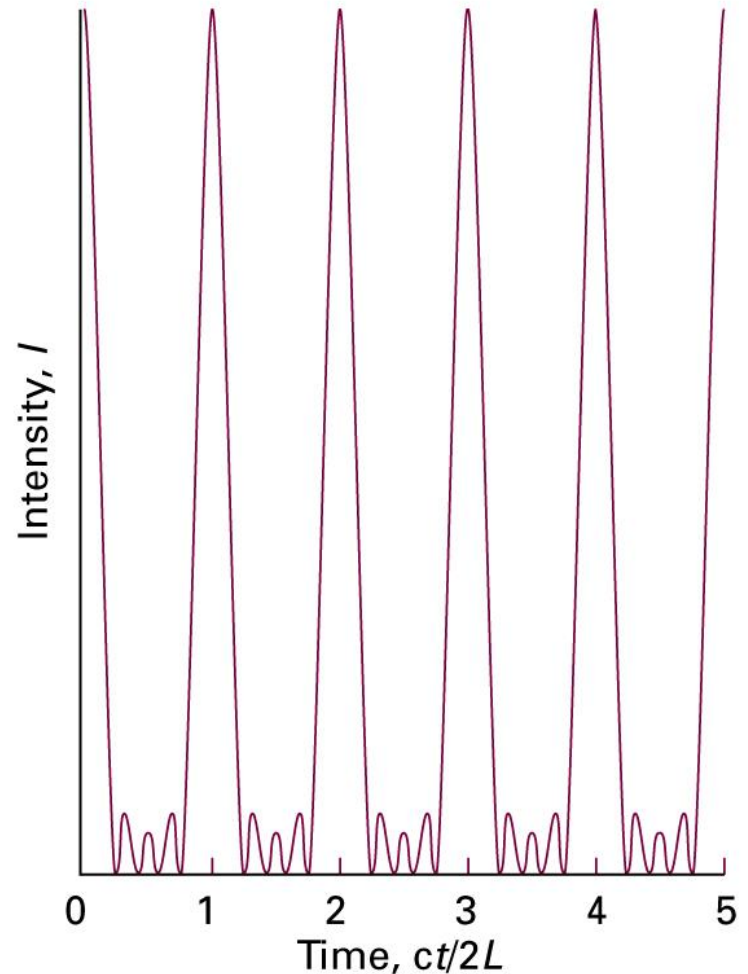peak interval: t=2L/c ⟵ $n \times \dfrac{1}{2}\lambda = L$

ex. when cavity length is 30 cm, t= 2ns.

peak becomes sharper as **<u>N is increased</u>**.

-the wider the range of modes superimposed, the narrower the pulses

$$I \propto E*E = E_0^2 \dfrac{\sin^2(N\pi ct/2L)}{\sin^2(\pi ct/2L)}$$

ex. when cavity length is 30 cm and 1000 modes contribute, pulse width is 4 ps.
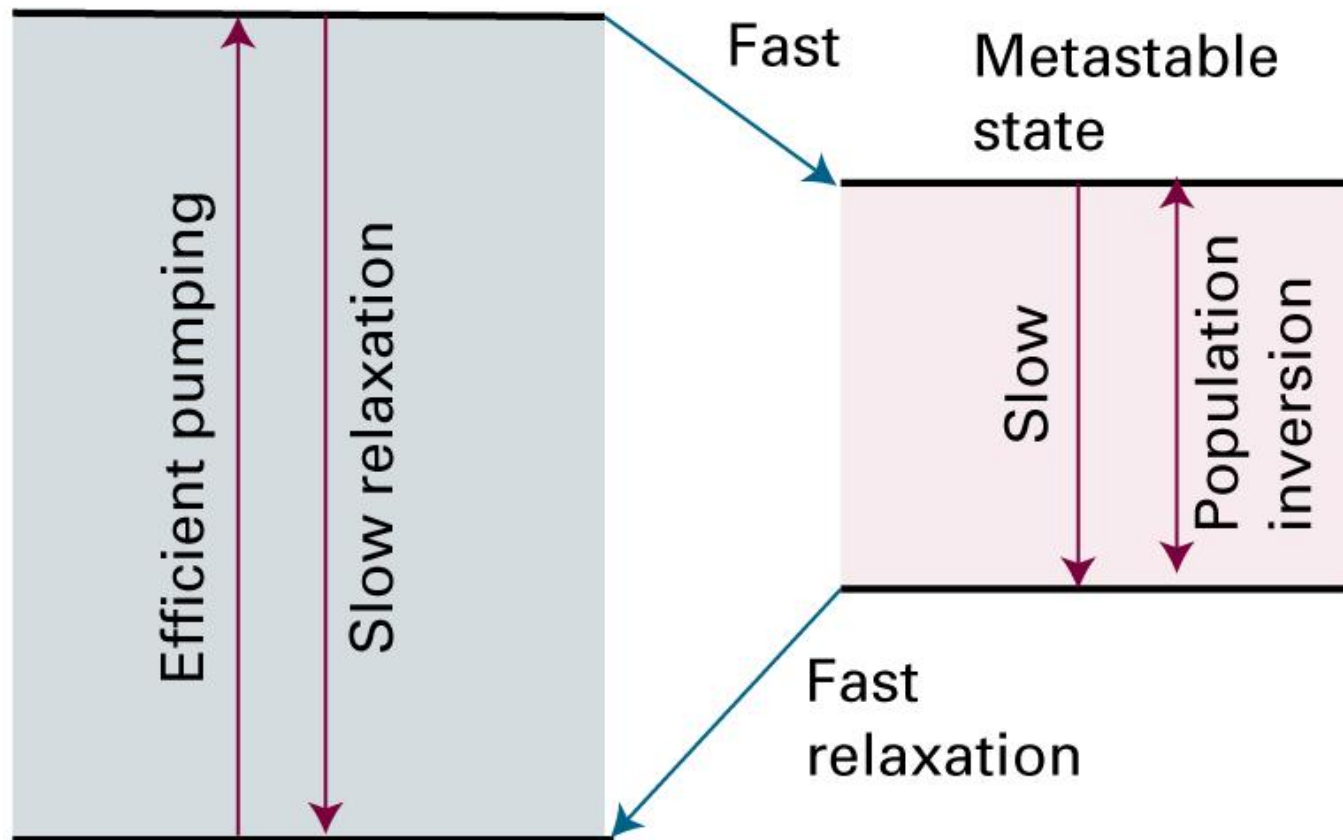

detailed structure of the pulsed generated by a mode-locked laser. (*Justification 13.5*)

Further information: Practical lasers

Depending on active medium,

- solid-state lasers

- gas lasers

- chemical and exciplex lasers

- Dye lasers

A summary of the features
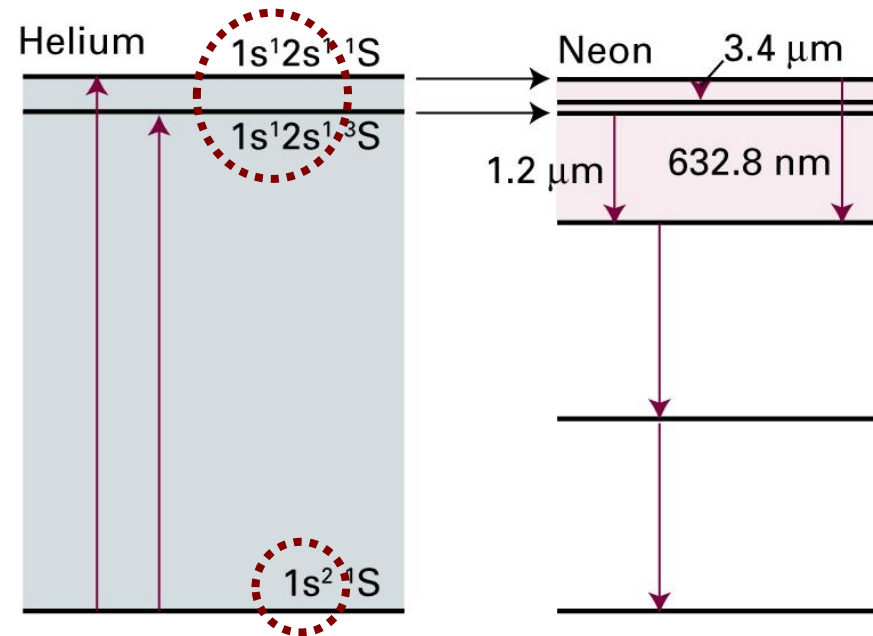needed for efficient laser action.
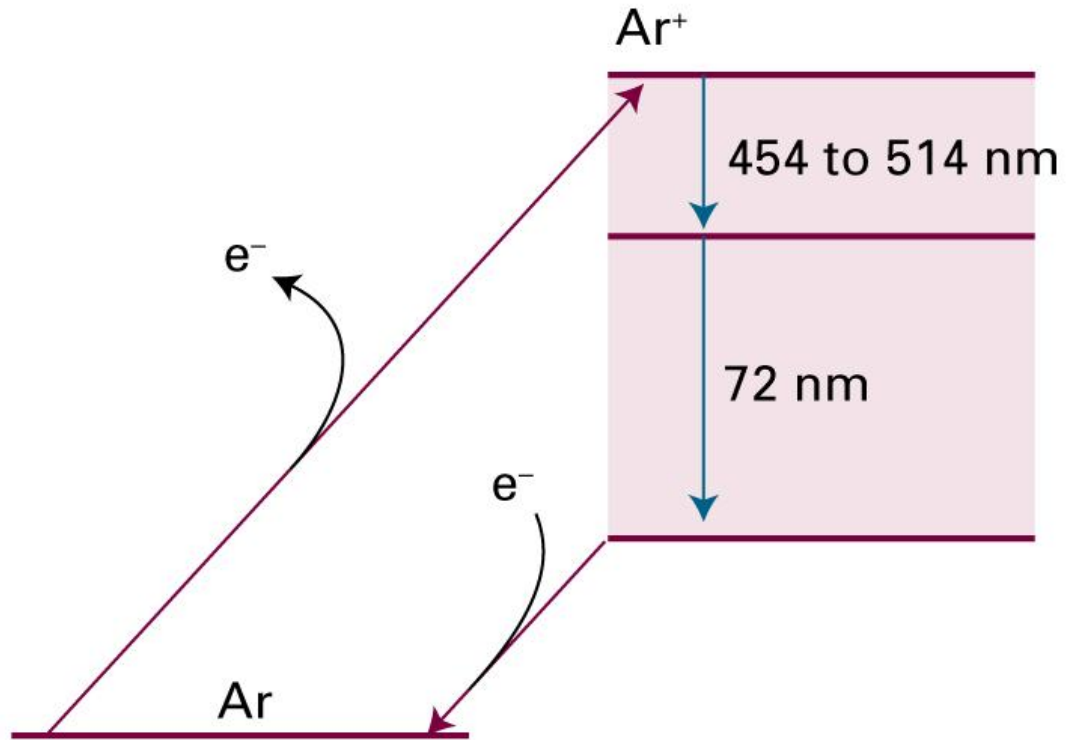
- gas lasers

-high power due to easy cooling

-**helium-neon** laser. (633 nm radiation)

The pumping (of the neon) depends on a coincidental matching of the helium and neon energy separations,

so excited He atoms can transfer their excess energy to Ne atoms during a collision.

Helium $1s^12s^1$ ^1S Neon   3.4 μm

$1s^12s^1$ ^3S

1.2 μm   632.8 nm

$1s^2$ ^1S

- **Ar ion** laser.

-**carbon dioxide laser**.

Most of the working gas is nitrogen.

The pumping: matching of energy separations;
the vibrationally excited N_2 molecules have excess energies that correspond to a vibrational excitation of the antisymmetric stretch of CO_2. (v_3)

the laser transition is
from $v_3=1$ to $v_1 =1$
(from lowest excited anti-symmetric stretch to lowest excited level of symmetric stretch)
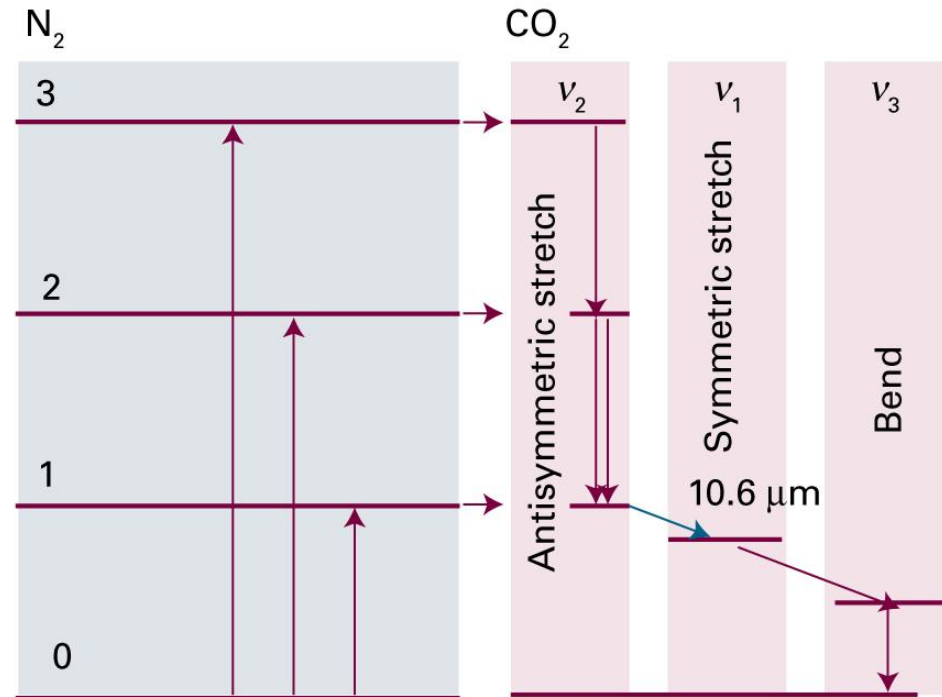
•Chemical and exciplex lasers

population inversion via chemical reaction
ex. photolysis of Cl_2 -> Cl attacks H_2 -> HCl and H
-> H attacks Cl_2 -> 'hot' HCl

•exciplex lasers

exciplex: AB*
excimer: AA* (excited dimer)

The molecular potential energy curves for an exciplex.
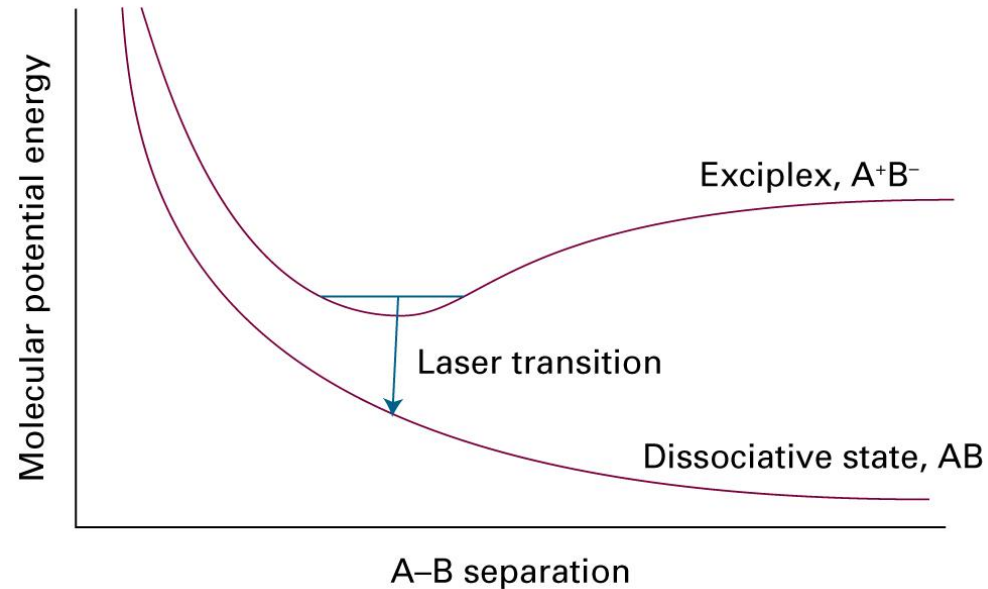
ex. dissociation of Cl_2 with Xe
-> Cl attacks Xe
-> XeCl* (life time 10 ns)
-> as soon as losing photon, XeCl dissociates

•Dye lasers

-Broad spectral characteristics of Titanium sapphire laser or dye laser

-The optical absorption spectrum of the dye Rhodamine 6G and the region used for laser action.