

# Electronic Transitions

Reading: Atkins, Ch. 14

→ several eV ( $> \sim 2$  eV)  
cf.  $1 \text{ eV} = 8065.5 \text{ cm}^{-1}$  or  $86.5 \text{ kJ/mol}$

## The Solid State

Ch 20. (pp.723-728)

- **Electronic spectroscopy:** visible or UV spectroscopy

- Absorption spectroscopy

at normal temperature

$$N_2/N_1 = \exp(-\Delta E/kT), \text{ at } 300 \text{ K } kT \sim 200 \text{ cm}^{-1}, \Delta E \sim 16000 \text{ cm}^{-1}$$
$$= \exp(-80) \sim 0$$

at 3000 K,  $kT \sim 2000 \text{ cm}^{-1}$ ,

$$N_2/N_1 = \exp(-8) \sim 3.4 \times 10^{-4}$$

→ almost ground states: “absorption”

- Emission spectroscopy: “luminescence”

fluorescence, phosphorescence, chemiluminescence

- **Parity** : g or u, symmetry, antisymmetry

behavior under inversion (i)  $x, y, z \rightarrow -x, -y, -z$

- same sign: g (gerade, even in German)

- opposite sign: u (ungerade)

$i1s\sigma \rightarrow 1s\sigma$  : g

$i1s\sigma^* \rightarrow -1s\sigma^*$  : u

**- Term symbols (for molecules)**

$\Lambda \hbar$ , component of total orbital angular momentum about the internuclear axis

$|\Lambda| = \Sigma, \Pi, \Delta, \Phi, \dots$  for  $|\Lambda| = 0, 1, 2, 3, \dots$

$\Lambda$  : the sum of  $\lambda$  for the individual electrons in a molecule

e.g., single electron in  $\sigma$  orbital:  $\lambda = 0 \rightarrow \Lambda = 0$  (term symbol of  $\text{H}_2^+$  is  $\Sigma$ )

- **Selection rules**

Removal of the center of symmetry:  
vibronically allowed transition  
(e.g., d-d transition)

- **Vibrational transitions accompanied by electronic excitation**

- Franck-Condon Principle

“Because the nuclei are so much more massive than the electrons, an electronic transition takes place very much faster than the nuclei can respond”

Electronic transition + vibrational lines:  
spectral band

No minimum of excited state:  
Dissociation of molecule:  
Continuous absorption band

e.g., 17.1



# **The electronic spectra of polyatomic molecules**

Chromophore: groups with characteristic optical absorptions

- d-d transitions

- Charge-transfer transitions

electron transfer from the ligands into the d orbitals of central atom

Electron transfer from d orbitals of central atom into the ligand

→ intense absorption

LMCT (ligand-to-metal charge transfer transition)

MLCT (metal-to-ligand charge transfer transition)

## The fates of electronically excited states

$$\tau_{\text{vib}} \sim 10^{-13} \text{ sec}, \tau_{\text{rot}} \sim 10^{-12} \text{ sec},$$
$$\tau_{\text{electronic}} \sim 10^{-15} \text{ sec} \text{ (much faster than vib/rot)}$$

$$R_e' > R_e \text{ (more antibonding character)}$$

• **Fluorescence (형광) & phosphorescence (인광): emission**

- Fluorescence: spontaneously emitted radiation ceases immediately after the exciting radiation is extinguished

- Phosphorescence: spontaneous emission may persist for long period

- Fluorescence: immediate conversion of absorbed radiation into re-emitted energy

(emissive transition occurs after some vibrational energy discarded)

- Phosphorescence: the storage of energy in a reservoir from which it slowly leaks  $\Rightarrow$  triplet excited state existed

intersystem crossing: singlet  $\rightarrow$  triplet

triplet  $\rightarrow$  singlet: spin forbidden, however, not totally forbidden because spin-orbit coupling (heavy atom effect (heavy atom favorable))  $\Rightarrow$  emission slowly and continuously

- Chemiluminescence: excited molecule → chemical reaction
- Dissociation and predissociation: excited molecule → breaking of bonds

- **Laser (light amplification by stimulated emission of radiation)**

Requirements:

1) existence of a metastable excited state (excited state with a long enough lifetime)

2) greater population in the metastable state than in the lower state → “population inversion” needed:

$N_2 > N_1$  (more molecules more molecules in the upper state than in the lower state)

at equilibrium:  $N_2/N_1 \ll 1 \Rightarrow$  by pumping: electric discharge

- three or four system

three-level system:

ineffective population inversion



- four-level system: higher population inversion

- laser action

ex. solid crystal (Ruby), SC,  
solution(dye), gas

⇒ “cavity”: particle-in-a box,  $n \times (1/2)\lambda = L$ ,  $n = 1, 2, \dots$ ,  $L$ : length of cavity:  
constructive, all other wavelengths destructive “resonant mode”

spontaneous emission → stimulated emission

coherent: no phase difference  
monochromatic, intense,  
directional (parallel)

- Q-switching: pulse of laser ( $\sim$  ns)

ex. saturable dye: many  
molecules excited by radiation:  
transparent

- mode locking: pulse of  $<$  ps

mode superimposing    sharp pulse peak

## - Examples of lasers

efficient laser

### 1) solid state lasers

- active lasing medium: single crystal or glass

- 1960 Ruby:  $\text{Al}_2\text{O}_3 + \text{Cr}^{3+}$  ion: three level laser: 694 nm radiation, pulse,  
continuous available

- neodymium, Nd:YAG:  $\text{Nd}^{3+} + \text{yttrium aluminum garnet } (\text{Y}_3\text{Al}_5\text{O}_{12})$ , four level laser, 1064 nm (IR) & 532 nm (after frequency doubling)

- Glass: cheap, weak, pulse only

cf. Nonlinear optical effects with lasers

dielectric medium (nonconductor (no free electron),  
optically transparent)

polarization (molecular distortion) of valence electron  
of molecules of medium

polarization  $P = \alpha E$ ,  $\alpha$ : constant,  $E$ : electric field “linear”

At high radiation intensities (e.g., laser) ( $E \rightarrow$  binding energy of the electron)

$$P = \alpha E + \beta E^2 + \gamma E^3 + \dots \quad \alpha > \beta > \gamma \quad \text{“nonlinear optical effect”}$$

If considering two terms,

$$P = \alpha E_m \sin \omega t + \beta E_m^2 \sin^2 \omega t \quad E_m: \text{max. amplitude}$$

Using  $\sin^2 \omega t = (1/2)(1 - \cos 2\omega t)$

$$\therefore P = \alpha E_m \sin \omega t + (\beta E_m^2 / 2)(1 - \cos 2\omega t)$$

normal linear term at high intensity  $\Rightarrow 2\omega$  (double) frequency radiation  
(low intensity)

$\therefore$  frequency double process: producing shorter wavelength

e.g., 1064 nm Nd:YAG  $\rightarrow$  532 nm (through dielectrics, potassium dihydrogen phosphate, 30 % yield)  $\rightarrow$  266 nm (UV) through ammonium dihydrogen phosphate

## 2) gas lasers

- 4 types:

a) neutral atom lasers, He-Ne

b) ion lasers,  $\text{Ar}^+$ ,  $\text{Kr}^+$

c) molecular lasers,  $\text{CO}_2$ ,  $\text{N}_2$

d) eximer

-He-Ne laser: He+Ne (5:1), 632.8 nm ,  
continuous

-  $\text{Ar}^+$  ion laser: ~ 1atm Ar, four-level, 488 to 514 nm

-  $\text{Kr}^+$  ion laser: wide range, 647 nm (red)

- molecular lasers

CO<sub>2</sub> laser: 1060 nm (900-1100 cm<sup>-1</sup>)

from vibrational transitions

N<sub>2</sub> laser: 337 nm (UV), pulse

3) Excimer lasers (Exciplex laser): gases mixture of He, F, one of rare gases (Ar, Kr, Xe)

rare gas excited & react with F to form excited ions (ArF<sup>+</sup>, KrF<sup>+</sup>, XeF<sup>+</sup>) “excimer”

→ stable only in the excited state

351 nm (XeF), 248 nm (KrF), 193 nm (ArF), pulse



#### 4) Dye lasers

- broad spectral characteristics (solvent broadens the vibrational structure)

e.g., Rhodamine 6G in methanol

- light emitting diodes & semiconductor lasers

p-n junction → light emitting diodes

-Si: largely in the form of heat

(indirect band gap (different linear momentum))

need to transfer momentum to the lattice: heat

→ GaAs: direct band gap (same linear momentum) : emit light

GaAs: IR, GaAs + phosphorous ( $\text{GaAs}_{0.6}\text{P}_{0.4}$ : red light)

$\text{Ga}_{1-x}\text{Al}_x\text{As}$ : CD player

- Applications of lasers

# Time-resolved spectroscopy

- **Photoelectron spectroscopy**

measure the ionization energies of molecules when electrons are ejected from different orbitals

photoelectron, ejected electron

- UPS (ultraviolet photoelectron spectroscopy)

detect valence electron: ionization energy of molecules from valence orbitals

radiation source: He(I) line,  $1s^1 2p^1 \rightarrow 1s^2$ , 58.43 nm (21.22 eV)

UPS of HBr, valence orbital (molecular orbital)

-XPS (X-ray): core electron

→ core orbital , surface sensitive, chemical shift...

“ESCA” (electron spectroscopy for chemical analysis)



# The band theory of solids (Ch.20)

- Extreme case of delocalization: solid
- Two type of solids
  - i) Metallic conductor:  $T \uparrow \rightarrow \text{conductivity} \downarrow$
  - ii) Semiconductor:  $T \uparrow \rightarrow \text{conductivity} \uparrow$ 
    - SC with very low electrical conductivities: insulator