

Electronic Transitions

Reading: Atkins, Ch. 14

→ several eV ($> \sim 2$ eV)
cf. $1 \text{ eV} = 8065.5 \text{ cm}^{-1}$ or 86.5 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 $|\Lambda| = 0, 1, 2, 3, \dots$

Λ : the sum of λ for the individual electrons in a molecule

e.g., single electron in σ orbital: $\lambda = 0 \rightarrow \Lambda = 0$ (term symbol of H_2^+ is Σ)

- **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 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 $P = \alpha E$, α : 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, Ar^+ , Kr^+

c) molecular lasers, CO_2 , N_2

d) eximer

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

- Ar^+ ion laser: ~ 1atm Ar, four-level, 488 to 514 nm

- Kr^+ ion laser: wide range, 647 nm (red)

- molecular lasers

CO₂ laser: 1060 nm (900-1100 cm⁻¹)

from vibrational transitions

N₂ 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⁺, KrF⁺, XeF⁺) “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, $1s^12p^1 \rightarrow 1s^2$, 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: $T \uparrow \rightarrow$ conductivity \downarrow

ii) Semiconductor: $T \uparrow \rightarrow$ conductivity \uparrow

SC with very low electrical conductivities: insulator