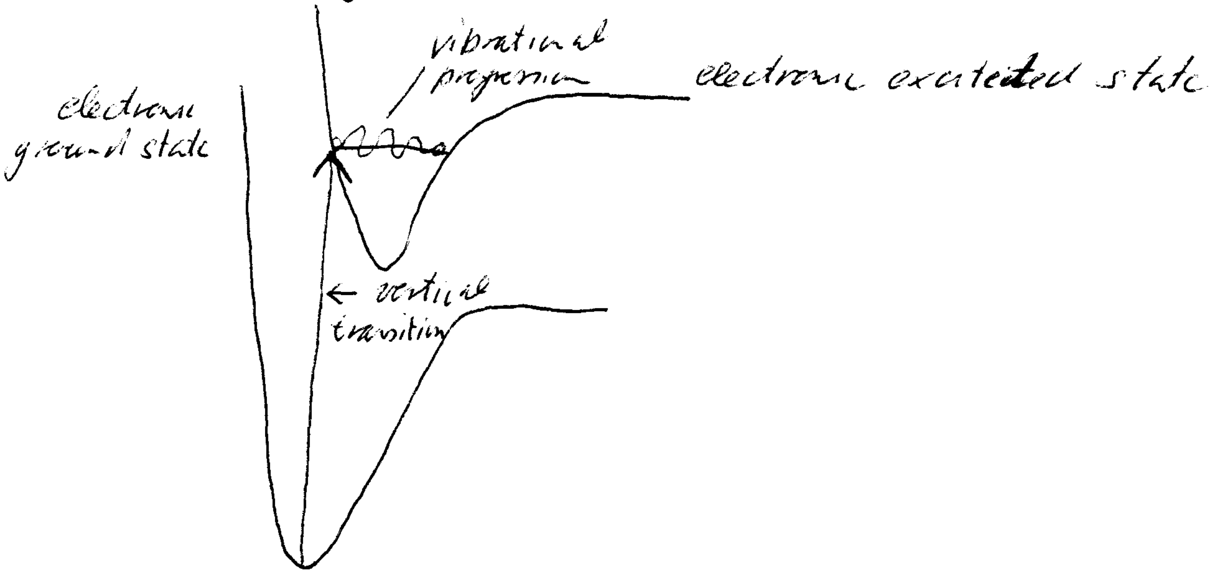
Spectroscopy, electronic transitions

no simple analytic expressions for the electronic energy levels of molecules!

parity — g gerade / u ungerade — under inversion

⇒ The only allowed transitions are transitions that are accompanied by a change of parity

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.



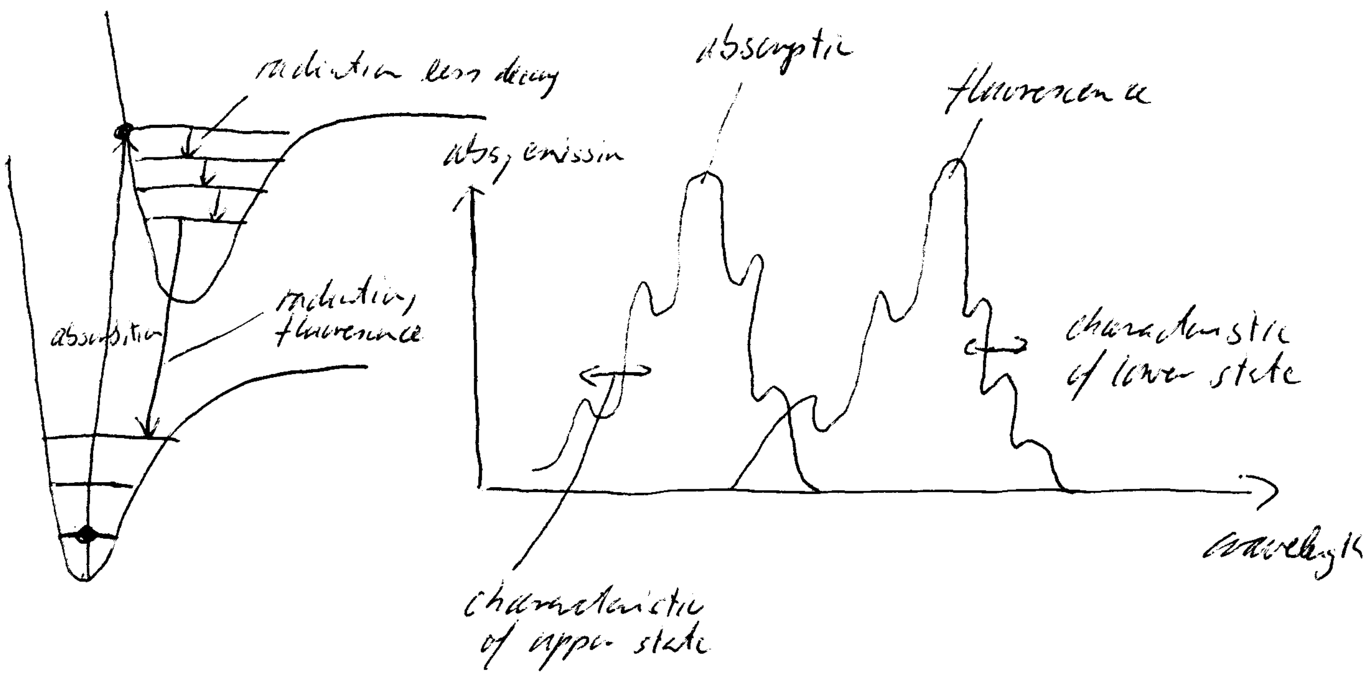
charge-transfer transitions:

- a complex may absorb radiation as a result of the transfer of an electron from the ligands into the d-orbitals of the central atom or vice versa
- electron moves through a considerable distance, which means that the transition dipole moment may be large ⇒ absorption is intense

fates of electronically excited states:

radiative decay process ⇒ photon
nonradiative ⇒ vibration, rotation, translation

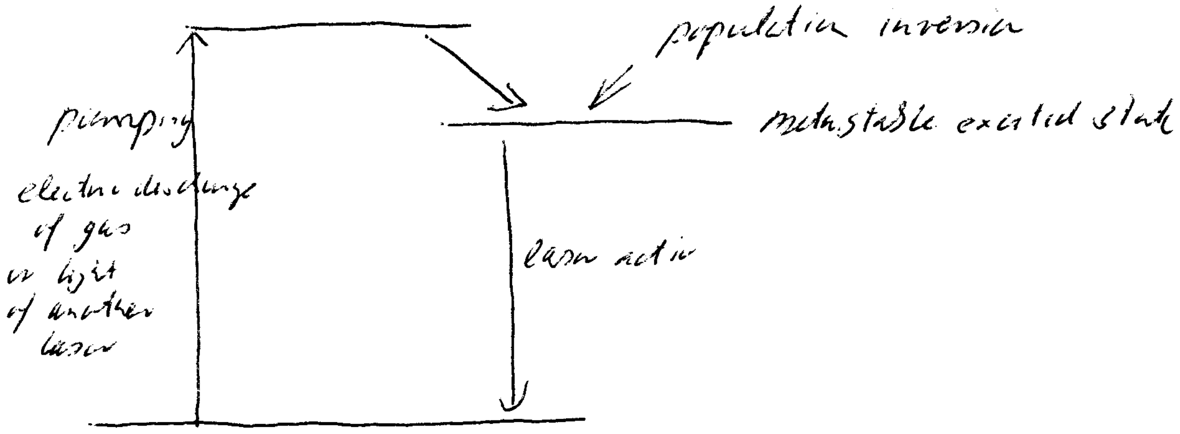
Fluorescence



phosphorescence: the same + intersystem crossing

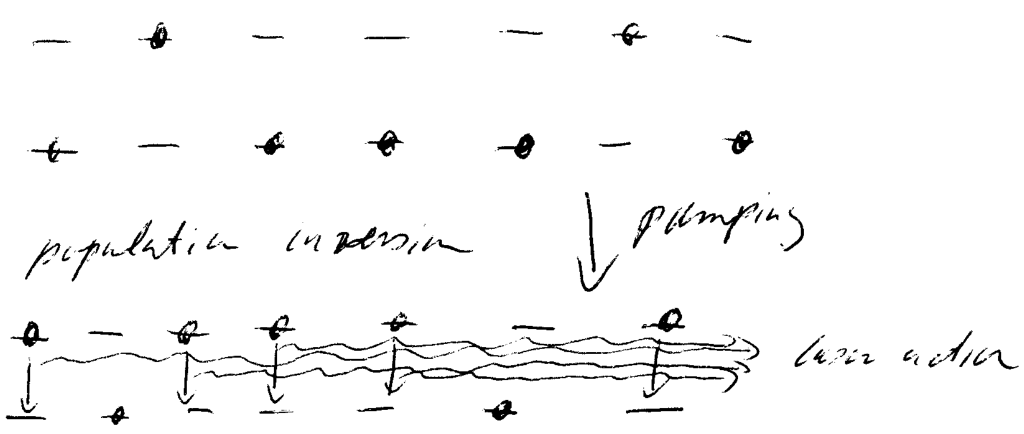
Lasers (→ Einstein)

general principles:



3-level laser

thermal equilibrium



Cavity:

two mirrors ⇒ interference $n \cdot \frac{1}{2} \lambda = L$ (L = length of cavity)

\+ interference compatible with laser medium

⇒ resonant modes

- light parallel to cavity, low divergence
- coherence: ~~spa~~ spatial coherence = in phase across the cross-section

coherence length l_c ⟸ temporal coherence = in phase along the beam coherence length l_c

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

$\Delta\lambda$: range of wavelengths present in the beam

light bulb: $l_c = 400nm$
He-Ne laser: $\Delta\lambda = 2pm$ $l_c = 10cm$

Q-switching:

laser can operate < continuously CW / pulsed PW

power concentrated into a brief pulse
⇒ Q-switching:

- achieve a population inversion in the absence of the resonant cavity
- plunge the population-inverted medium into cavity

⇒ integrate Pockels cell in laser cavity

Pockels cell converts plane-polarized light to circularly polarized light when an electrical potential difference is applied ⇒ no stimulated emission

Mode-locking:

⇒ picosecond pulses

- resonant modes differ in frequency by multiples of $c/2L$
- lock phases of resonant modes
  ⇒ sharp peaks, picosecond bursts
- achieved by varying the Q-factor of the cavity periodically at the frequency $c/2L$

resonant modes

$$E_n(t) = E_0\, e^{2\pi i(\nu + \frac{nc}{2L})t}$$

$$E(t) = \sum_n E_n(t) = E_0\, e^{2\pi i \nu t} \sum_{n=0}^{N-1} e^{i\pi n c t/L}$$

$$= E_0\, e^{2\pi i \nu t} \frac{\sin \frac{N\pi c t}{2L}}{\sin \frac{\pi c t}{2L}} \cdot e^{(N-1) i\pi c t/2L}$$

$$\Rightarrow \quad I \sim E_0^2 \frac{\sin^2 \frac{N\pi c t}{2L}}{\sin^2 \frac{\pi c t}{2L}}$$

⇒ peaks with maxima separated by $t = \frac{2L}{c}$

laser types:

1. Solid-State laser

active medium is a crystal or a glass

- Nd-YAG-Laser

  Nd^{3+} in yttrium aluminium garnet

  $\lambda = 1064$ nm

- titanium sapphire laser

  Ti^{3+}-ions in a crystal of sapphire (Al_2O_3)

  pumped by Nd-YAG laser

  $\lambda = 700$ nm $- 1000$ nm   vibronic laser

  broad absorption band at 500 nm that arises from vibronically allowed d-d transitions

- laser diodes!

2. Gas lasers

- helium-neon lasers (ratio 5:1)

  excitation of He-atom by electric discharge

  ⇒ He-Ne collision transfer of energy to Ne

- argon-ion laser
- krypton-ion laser

3) Chemical and exciplex lasers
4) Dye lasers