Physical Chemistry

Chem 131B

11: Electronic Spectroscopy
Big picture: spectroscopy

Quantum number = $\varepsilon$

Rotational transitions $\sim 1 \text{ cm}^{-1}$
Vibrational transitions $\sim 100-1000 \text{ cm}^{-1}$
Electronic transitions $\sim 10^4 \text{ cm}^{-1}$

Quantum number = $v$

Quantum number = $J$
Electronic spectroscopy

quantum number = $\varepsilon$

$E^*$

$v = 3$

$v = 2$

$v = 1$

$v = 0$

$J = 0, 1, 2, \ldots$

Electronic transitions are more energetic than vibrational and rotational transitions.

$E^o$

$v = 3$

$v = 2$

$v = 1$

$v = 0$

$J = 0, 1, 2, \ldots$

The rotational transitions sometimes don’t show up in the electronic spectra due to lack of resolution.
What happens to excited states?

**Non-radiative decay (heat)**
- Energy goes into molecular translations, vibrations, rotations

**Dissociation**
- Molecule falls apart

**Fluorescence**
- Radiation of a longer wavelength is emitted (ns timescale)

**Phosphorescence**
- Radiation of a longer wavelength is emitted (longer timescale)
Copper (II) sulfate (hydrated)

Thanks to Andreas Ehnbom for suggesting this example.
Copper (II) sulfate in solution

This molecule absorbs in the visible region due to d-d transitions.

We see the complementary color to what is absorbed.
Atomic orbitals

In a free atom, all the d-orbitals are degenerate.
**d-metal complexes**

In a d-metal complex, the degeneracy is broken.

d-d transitions occur between the ligand and the central atom.

The energy gap corresponds to visible light.
Plant pigments absorb strongly in the visible region. Chlorophyll a and β-carotene are examples of organic chromophores. The diagram shows the absorption spectra of chlorophyll a, chlorophyll b, and carotenoids across different wavelengths of light (400-700 nm).
Absorption spectroscopy

The Beer-Lambert law relates transmitted intensity at a given frequency to the path length and the sample concentration.

\[ I = I_0 10^{\varepsilon [J] \ell} \]

- \( I \) = transmitted intensity
- \( I_0 \) = incident intensity
- \( \varepsilon \) = molar absorption coefficient in \( \text{dm}^3\text{mol}^{-1} \text{cm}^{-1} \) or \( \text{cm}^2/\text{mol} \)
- \( [J] \) = concentration of species J in \( \text{mol/L} \)
- \( \ell \) = path length

\[ A = \log \frac{I_0}{I} \]

\[ A = \varepsilon [J] \ell \]

For an absorption band spread over a range of wavenumbers:

\[ A = \int_{\text{band}} \varepsilon (\tilde{\nu}) d\tilde{\nu} \]
Structural colors

The quarter-wave stack acts as a wavelength-specific reflector.
Membrane protein sensors

Chemoreceptors

Electric field receptors

Photoreceptors

Mechanoreceptors

Thermoreceptors
G-protein coupled receptors

Eye anatomy

http://www.olympusmicro.com/primer/lightandcolor/humanvisionintro.html
Rod cells and vision

http://www.olympusmicro.com/primer/lightandcolor/humanvisionintro.html
Rhodopsin

rod cells

retinal

Structure from www.ks.uiuc.edu/Research/rhodopsin/
Rhodopsin

Rhodopsin

Visual perception
Electronic motion is much faster than nuclear motion such that they are separable:

\[ \hat{H}_\varepsilon \psi_\varepsilon (r_i, R_j) = E_\varepsilon \psi_\varepsilon (r_i, R_j) \quad \text{electrons (electronic transitions)} \]

\[ \hat{H}_{\nu, J} \psi_{\nu, J} (R_j) = E_{\nu, J} \psi_{\nu, J} (R_j) \quad \text{nuclei (vibration, rotation)} \]

The probability of electronic transitions (related to overlap of the states) depends on the positions of the nuclei.
I$_2$ energy levels

- $\nu = $ vibrational quantum number
- $\tilde{\nu} = $ vibrational frequency
- $D_0 = $ dissociation energy
- $D_e = $ equilibrium dissociation energy
- $T_e' = $ electronic energy
- $\tilde{x}_e' = $ anharmonicity constant
- $(\nu' = b) = $ convergence limit