Fluorescence and Phosphorescence

Lecture 24

www.physics.uoguelph.ca/~pgarrett/Teaching.html
Review of L-23

- Energy levels in molecules
  \[ E_{n,v,J} = E_n + E_v + E_J \]
  where \( E_n \) is the electronic energy, \( E_v \) the vibrational energy, and \( E_J \) the rotational energy.

- Energy hierarchy
  \[ E_n \gg E_v \gg E_J \]

- \( E_n \) often in the visible range, \( E_v \) in the IR range, \( E_J \) in the microwave range.
Review of L-23

- Vibrational energy with \( \nu = 0,1,2,3,\ldots \)
  \[
  E_v = (\nu + \frac{1}{2})\hbar \omega = (\nu + \frac{1}{2})\hbar f
  \]
  \[
  \omega = \sqrt{\frac{k}{m_{\text{eff}}}}
  \]
- Rotational energy with angular momentum \( J = 0,1,2,3,\ldots \)
  \[
  E_J = \frac{\hbar^2}{2\Sigma} J(J + 1)
  \]
- All electronic states have vibrational levels built on them, and all vibrational states have rotational levels built on them
Photoluminescence

- Molecules that have an electronic excitation are *excited*
- Molecules that have a vibrational excitation are *hot*
- With light absorption, molecules may become *hot* and *excited*
- Physical process that leads to excited molecules can be *physical* (e.g. absorption of light), *mechanical* (e.g. friction), or *chemical* (e.g. reactions)
- When excited molecular states decay back to the ground state, resulting in the emission of light, they are undergoing a *luminescence* process
- Generation of excited molecules by light absorption, that then decay emitting visible light, is *photoluminescence*
- Photoluminescence processes are divided into 2 classes:
  - *Fluorescence* and *Phosphorescence*
Fluorescence

- Property of some atoms or molecules to absorb light at a particular wavelength and then emit light at a longer wavelength (lower frequency) than the incident light.

π electronic state $n+1$

Visible or UV radiation

π electronic state $n$

Only one of these transitions happens at any given time.

Visible radiation
- longer wavelength on average than incident

IR radiation

IR radiation

ν
3
2
1
0
Fluorescence

- Absorption process occurs over short time interval ($10^{-15}$ s) and does not change the direction of the $e^-$ spin
- *Vibrational relaxation* (emission of IR while lowering vibrational state) occurs in $\sim 10^{-12}$ s
- De-excitation to electronic ground state with emission of lower frequency light and IR occurs in $10^{-9}$ s
- Because vibrational relaxation occurs $\sim 1000$ times faster than de-excitation, most molecules return to a low-vibrational state before the de-excitation takes place
  - Emitted wavelengths nearly independent of incident radiation
- Shift in wavelength between absorption and emission spectra is the *Stokes shift*
Phosphorescence

- In the fluorescence process, the electron did not change its spin direction
- But under the appropriate conditions, a spin-flip can occur

Spin singlet

No spin flip

Spin triplet

Spin flip

- Spin flip can occur during absorption, or afterwards
Phosphorescence

- The situation where no spin flip occurs, the molecule is in a singlet state.
- When the electron undergoes a spin-flip, a triplet state is created.

![Diagram showing singlet and triplet states with transitions to ground state and excited state with longer wavelength radiation.](image_url)
Phosphorescence

• The light emission process must wait until electron undergoes a spin-flip to revert back to its original state
  – May take $10^{-3} – 10^2$ s
  – Light emission is delayed long enough so that materials “glow in the dark” after exposure to light
  – Because of the lower energy of triplet state, lower energy photon emission than incident or fluorescence photons

• Because of the long lifetimes, molecular triplet states are more often involved in photo-chemical and photo-biological reactions than singlet states in molecules
Fluorescence spectrophotometer

- Measure the intensity of fluorescence light as a function of wavelength
- Light source perpendicular to detector

- tungsten lamp – produces white light + UV + IR
- light source
- sample
- monochromator – extracts a very narrow wavelength band
- detector
- measures light intensity from sample