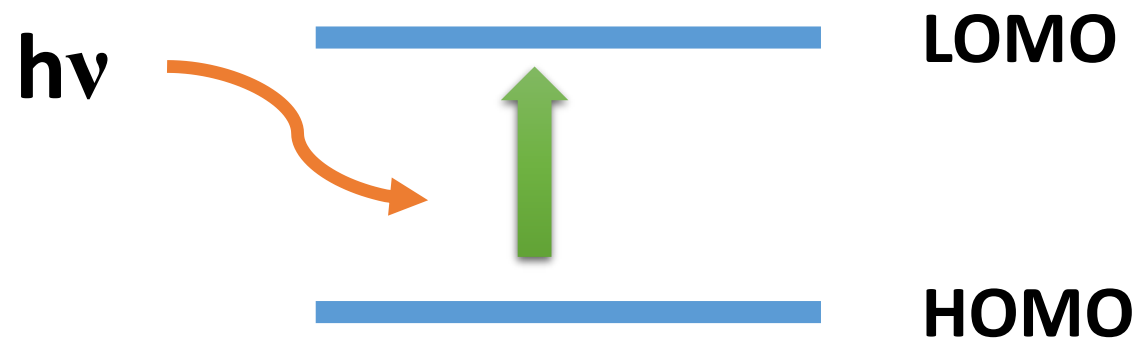
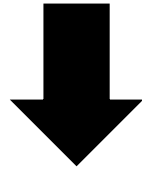


Materials Chemistry III

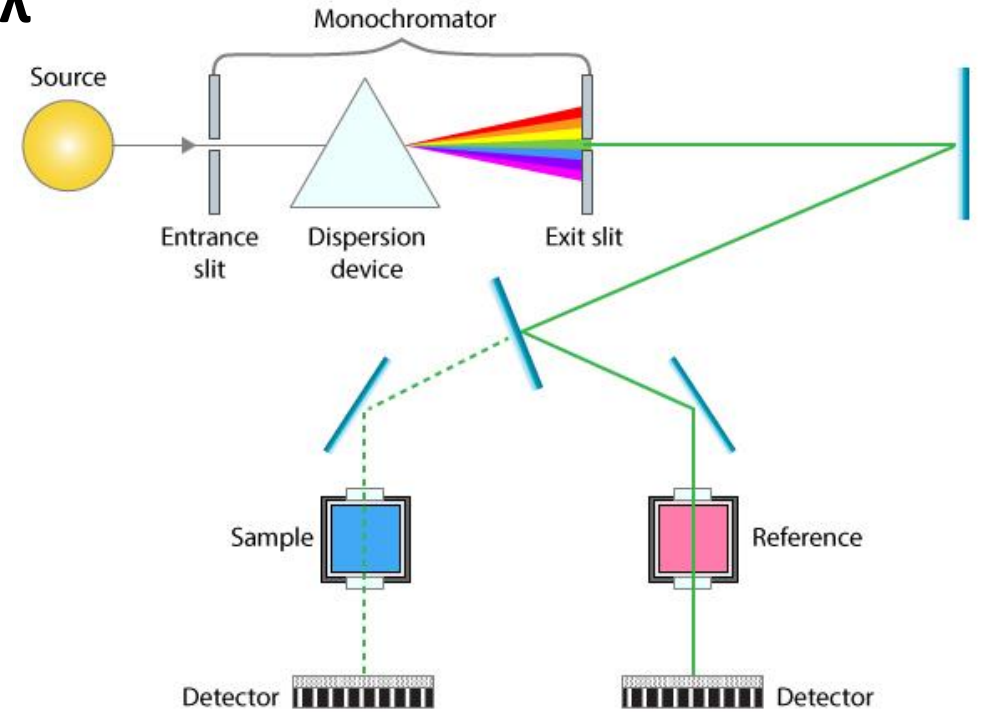
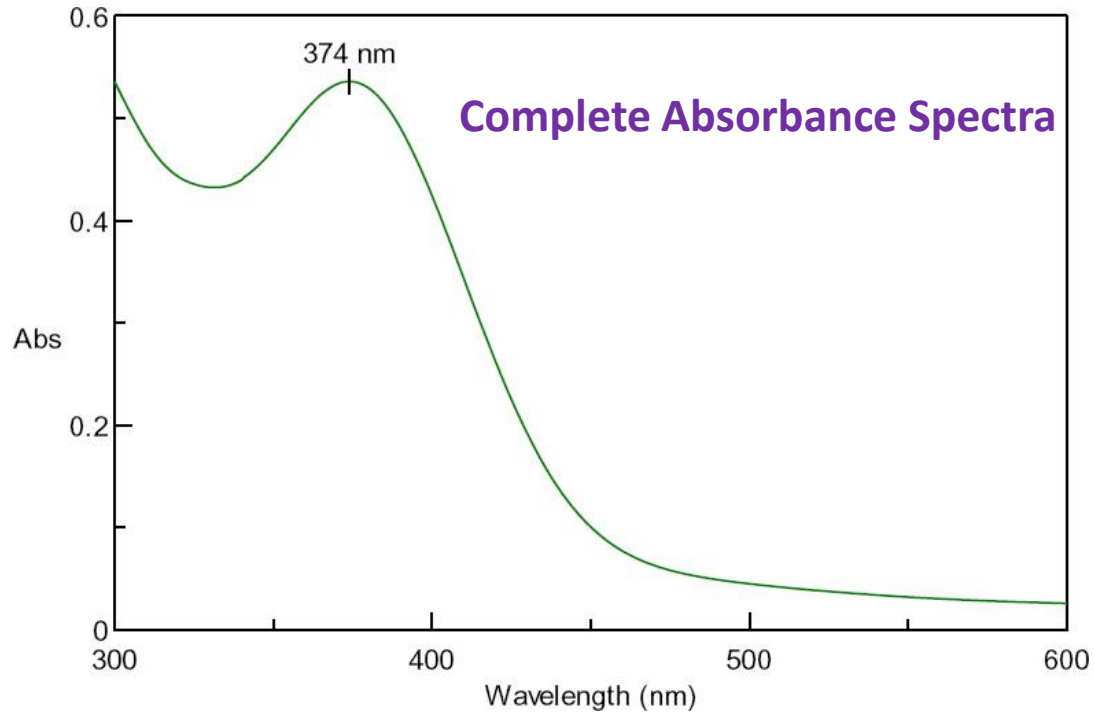
Day 10



Lambert-Beers law: $\log(I_0/I_t) = \epsilon c L = \text{Absorbance}$



Absorbance at various ' λ '



Energy sources

Renewable energy sources are naturally replenished.



Solar Energy



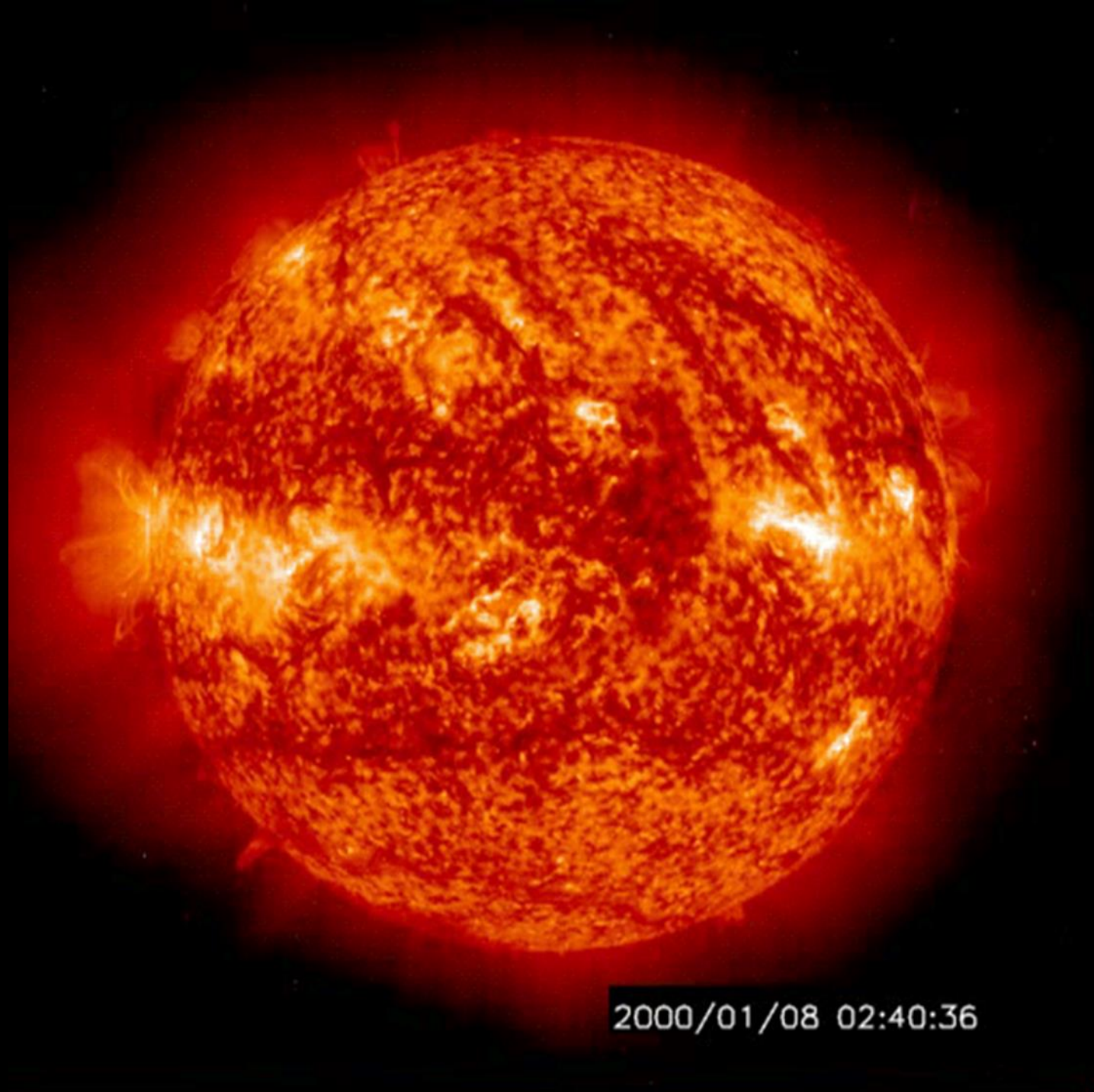
Wind Power



Tidal Waves

Geothermal Heat
Rain water

Green Resources



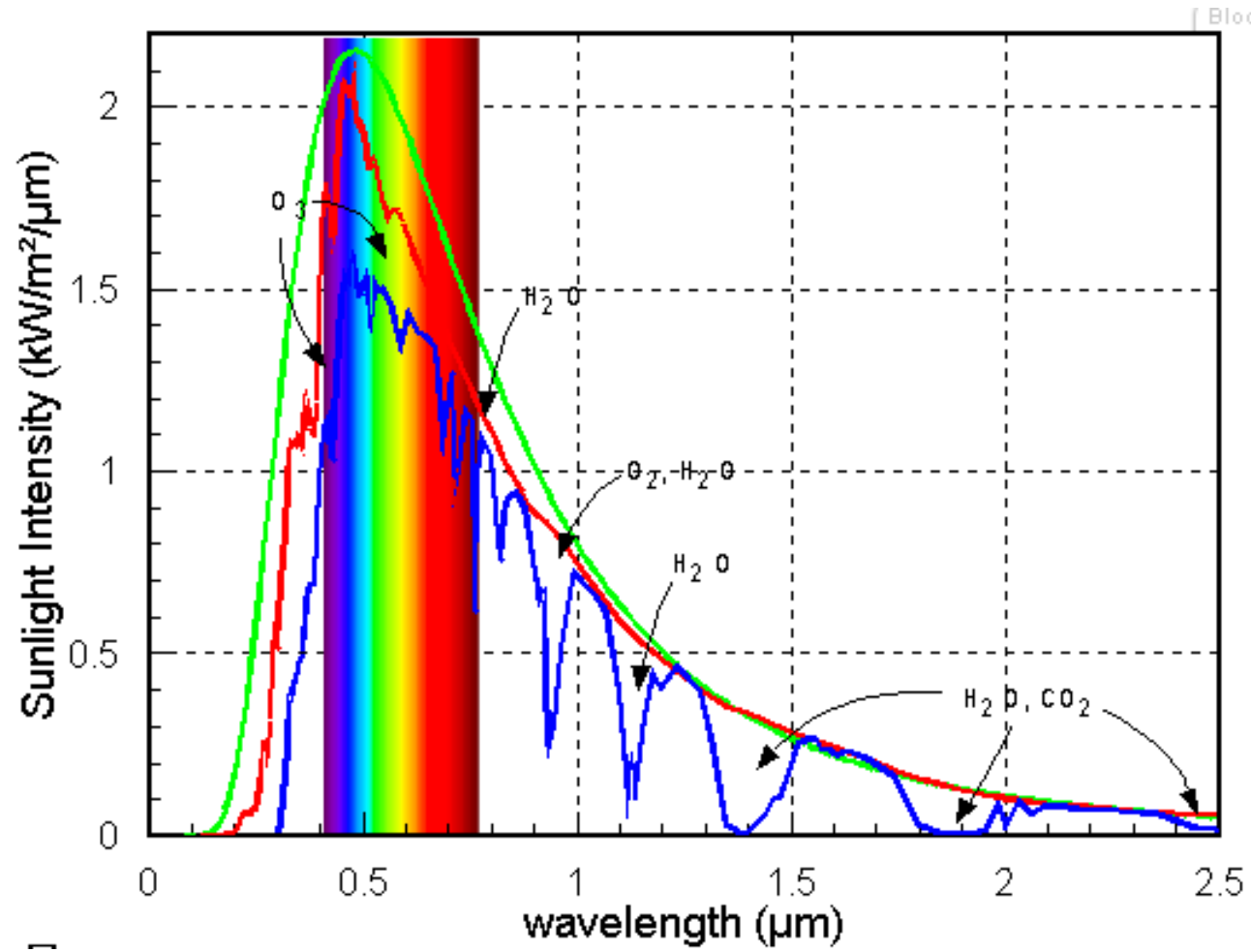
Comparative
Size of the earth



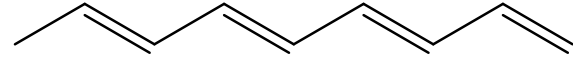
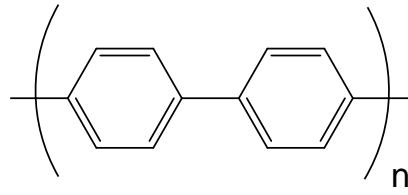
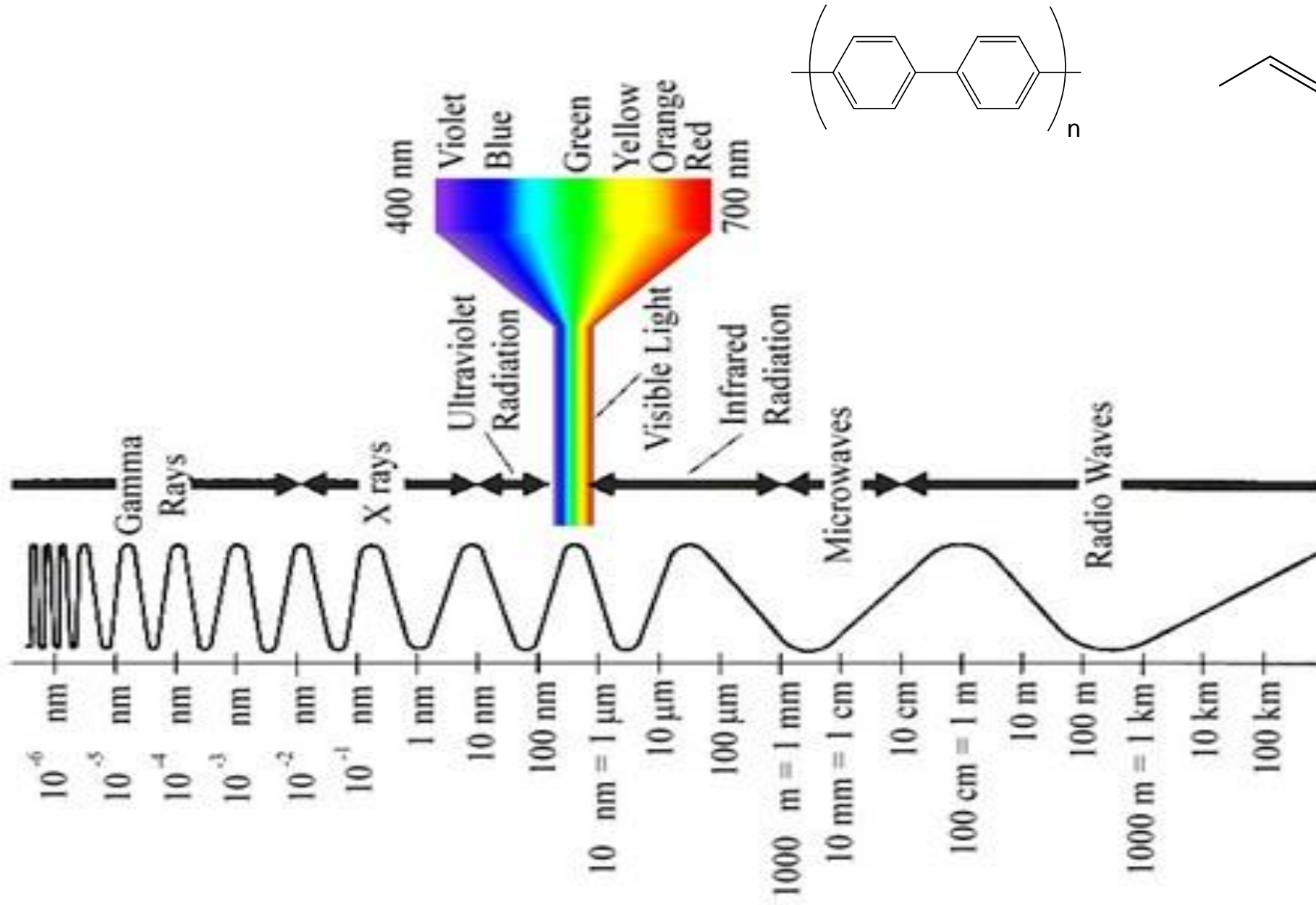
2000/01/08 02:40:36

* from National Oceanic
and Atmospheric
Administration - NASA

Solar spectra



**Black-body
Radiation**

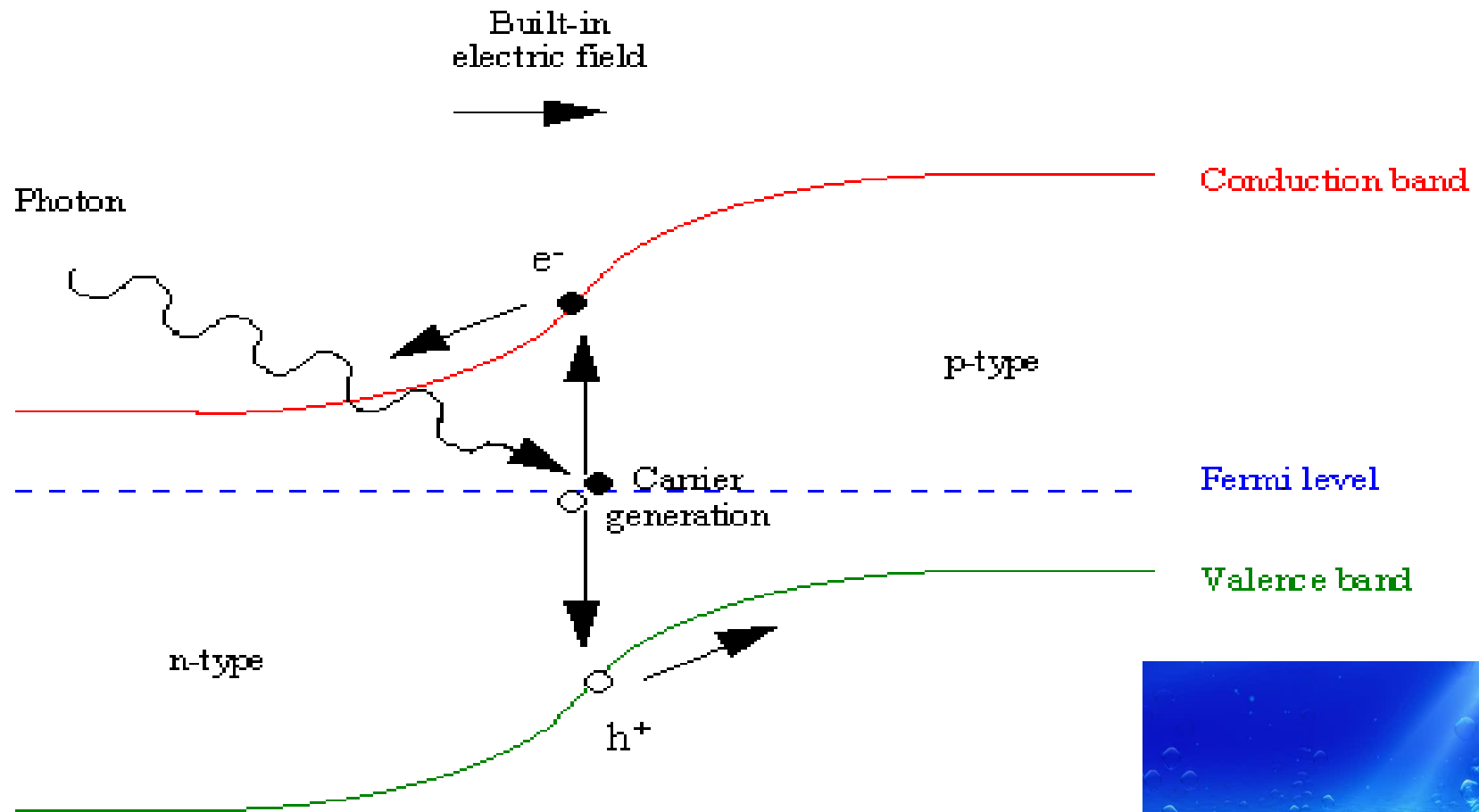


3.17 eV  1.8 eV

	<i>Violet</i>	<i>~ 3.17 eV</i>
	<i>Blue</i>	<i>~ 2.73 eV</i>
	<i>Green</i>	<i>~ 2.52 eV</i>
	<i>Yellow</i>	<i>~ 2.15 eV</i>
	<i>Orange</i>	<i>~ 2.08 eV</i>
	<i>Red</i>	<i>~ 1.62 eV</i>

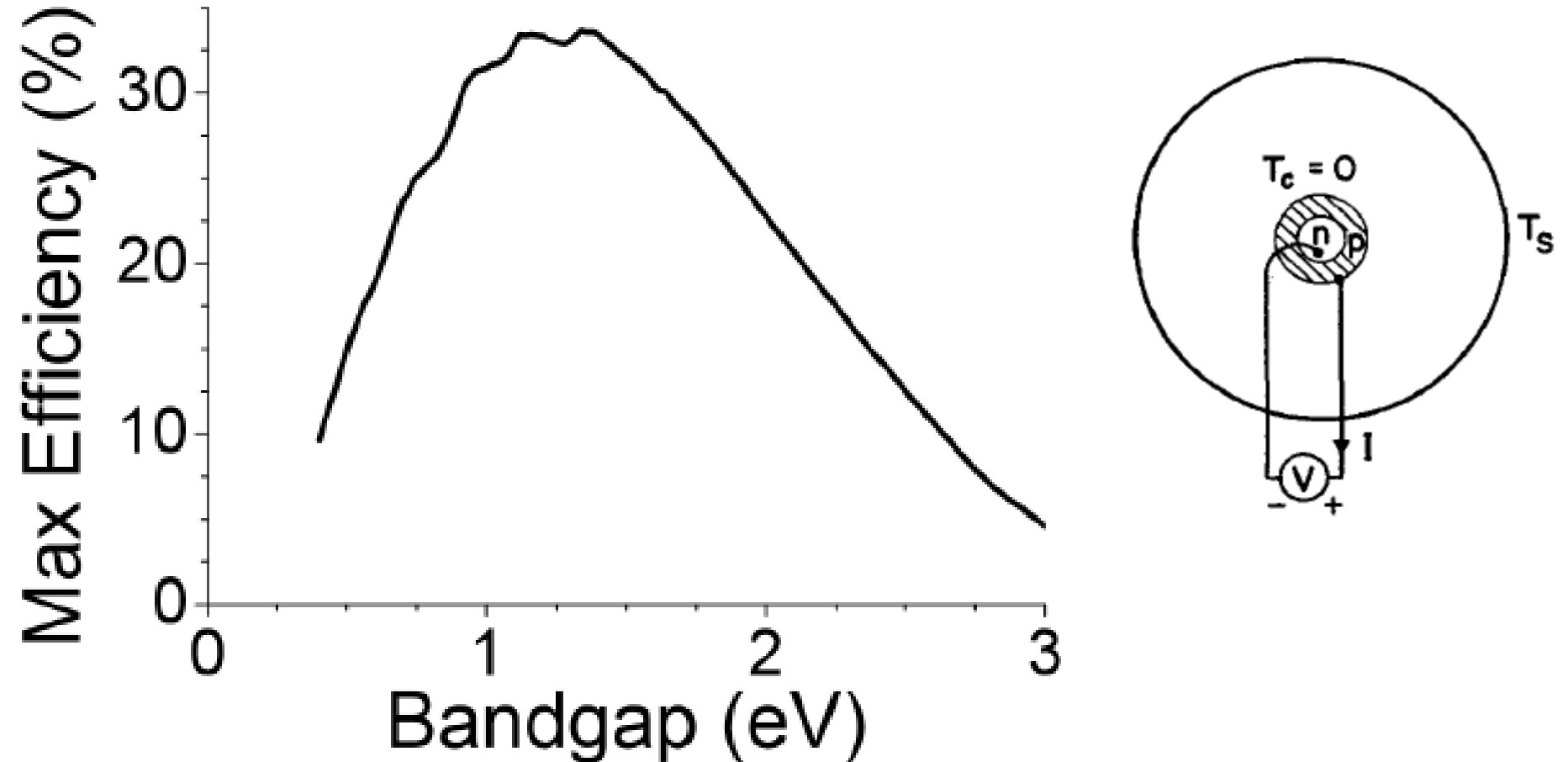
Human Eye : 450 nm to 650 nm

Solar cell



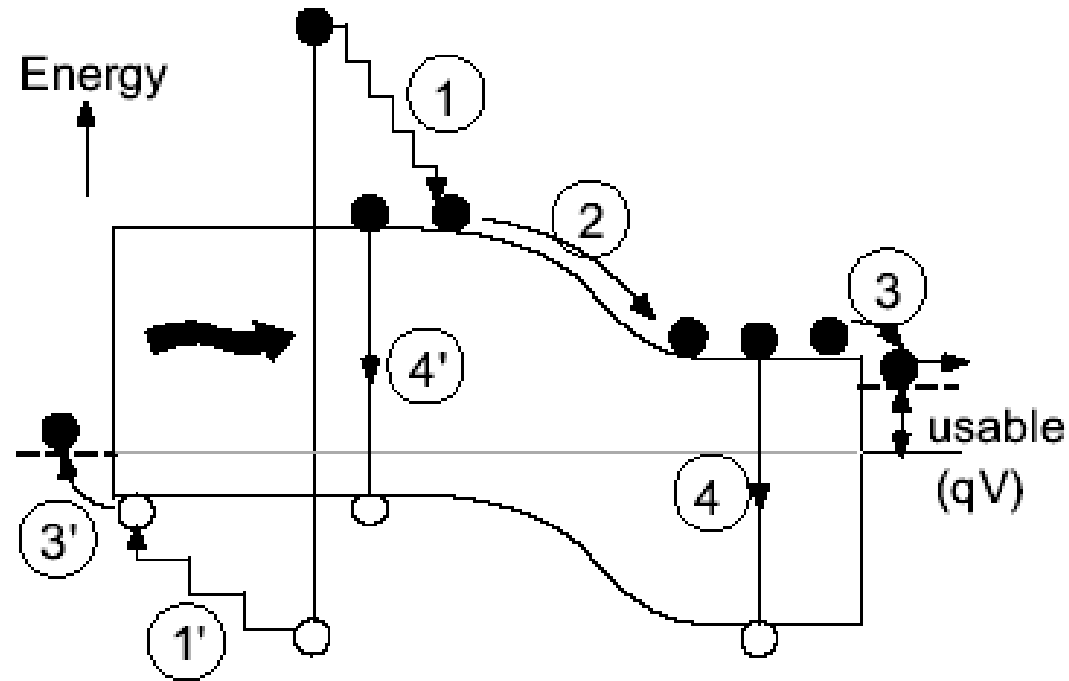
Detailed Balance Limit of Efficiency of p-n Junction Solar Cells

William Shockley, and Hans J. Queisser



The maximum efficiency of a **single junction solar-cell** was calculated by considering incident solar spectrum as a black body operated at 6000 K.

Efficiency Losses in Solar Cell



1 = Thermalization loss

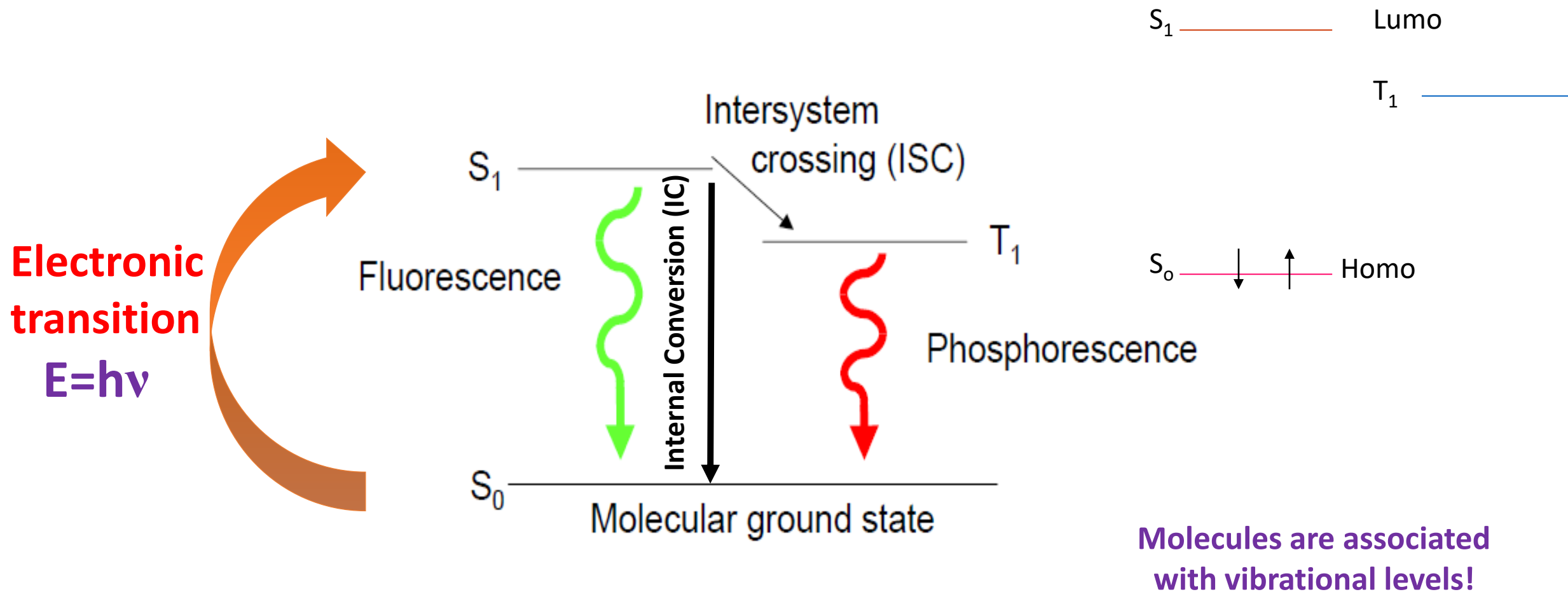
2 and 3 = Junction and contact voltage loss

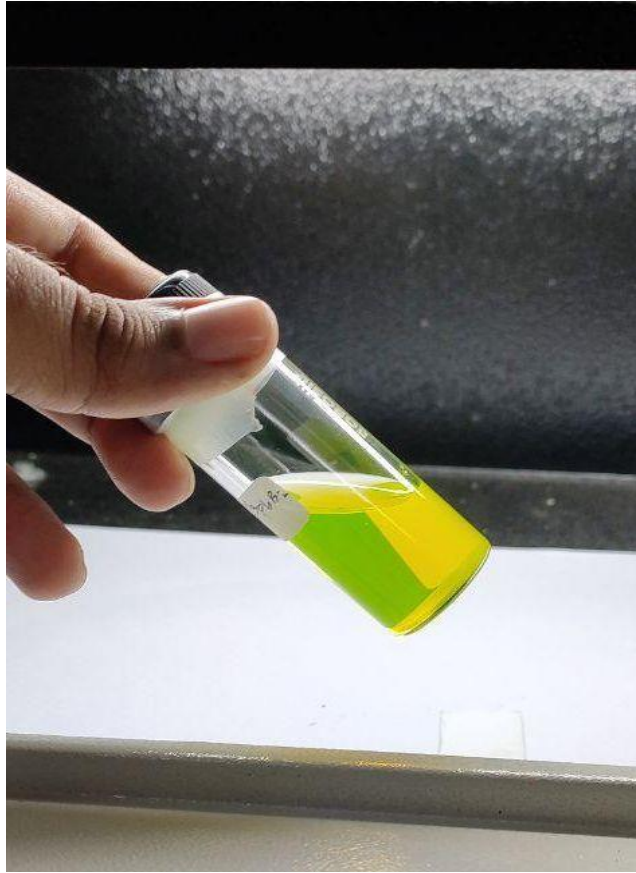
4 = Recombination loss

- 1. Excited State Electron Dynamics.**
- 2. Simple Harmonic Oscillator.**
- 3. Vibrational Levels.**

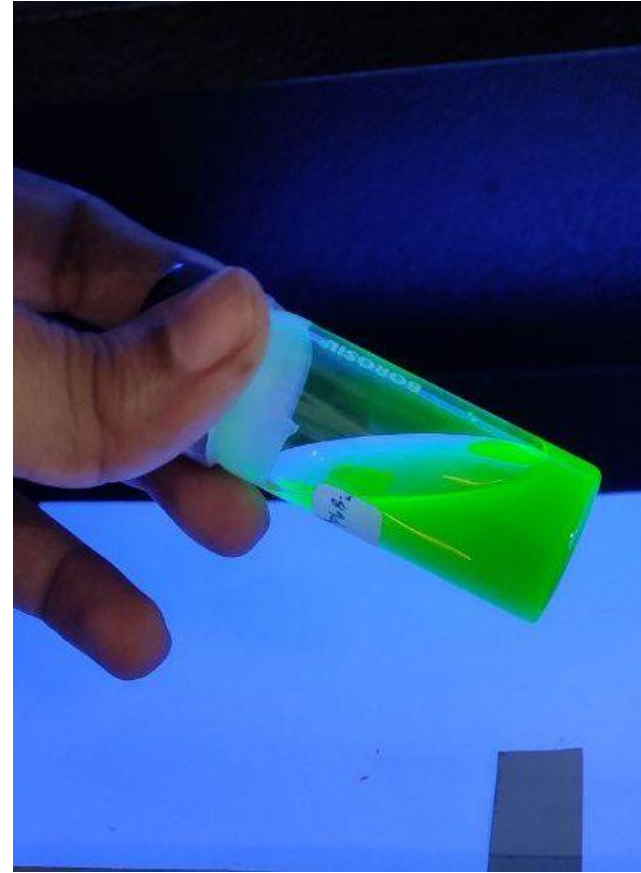
Excited State Kinetics

Electronic Structure of Conjugated Systems-Simple Diagram!



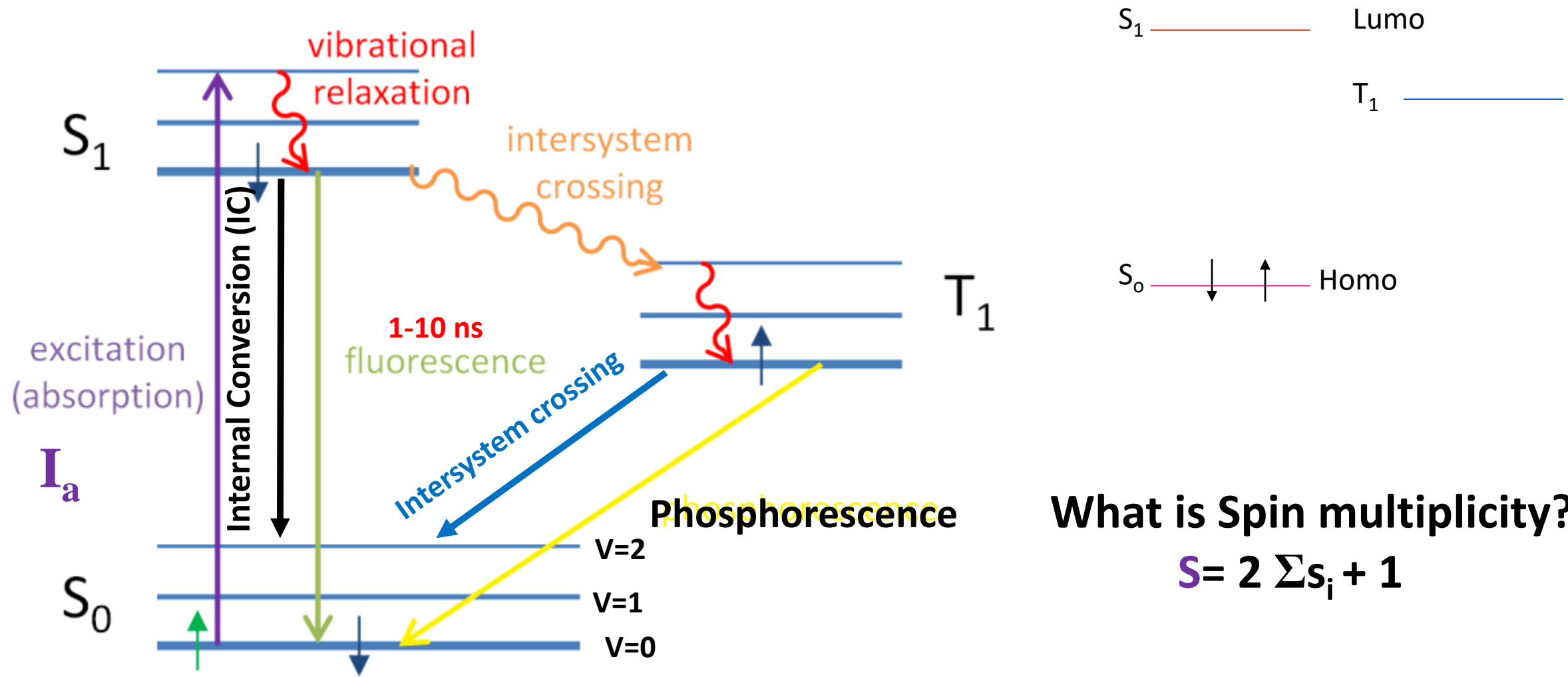


Under Visible light



Under UV-light

Electronic Structure of Conjugated Systems-Jablonski Diagram



What is Spin multiplicity?

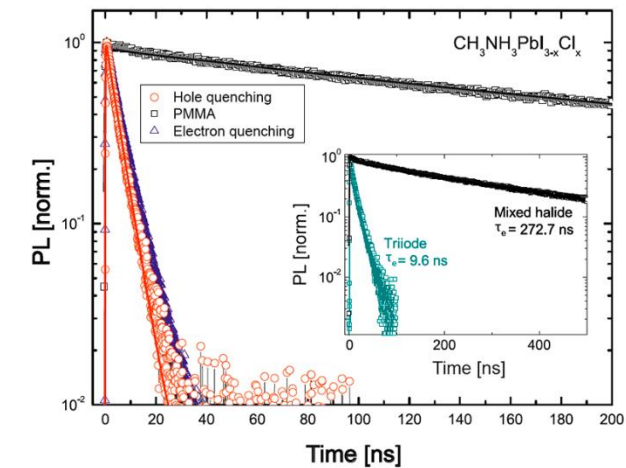
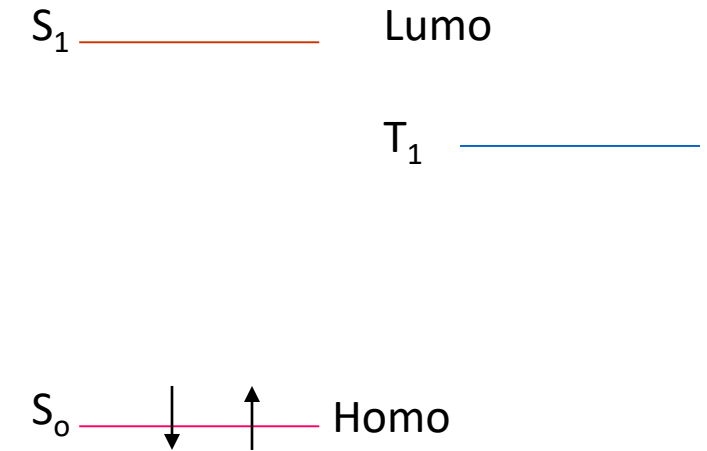
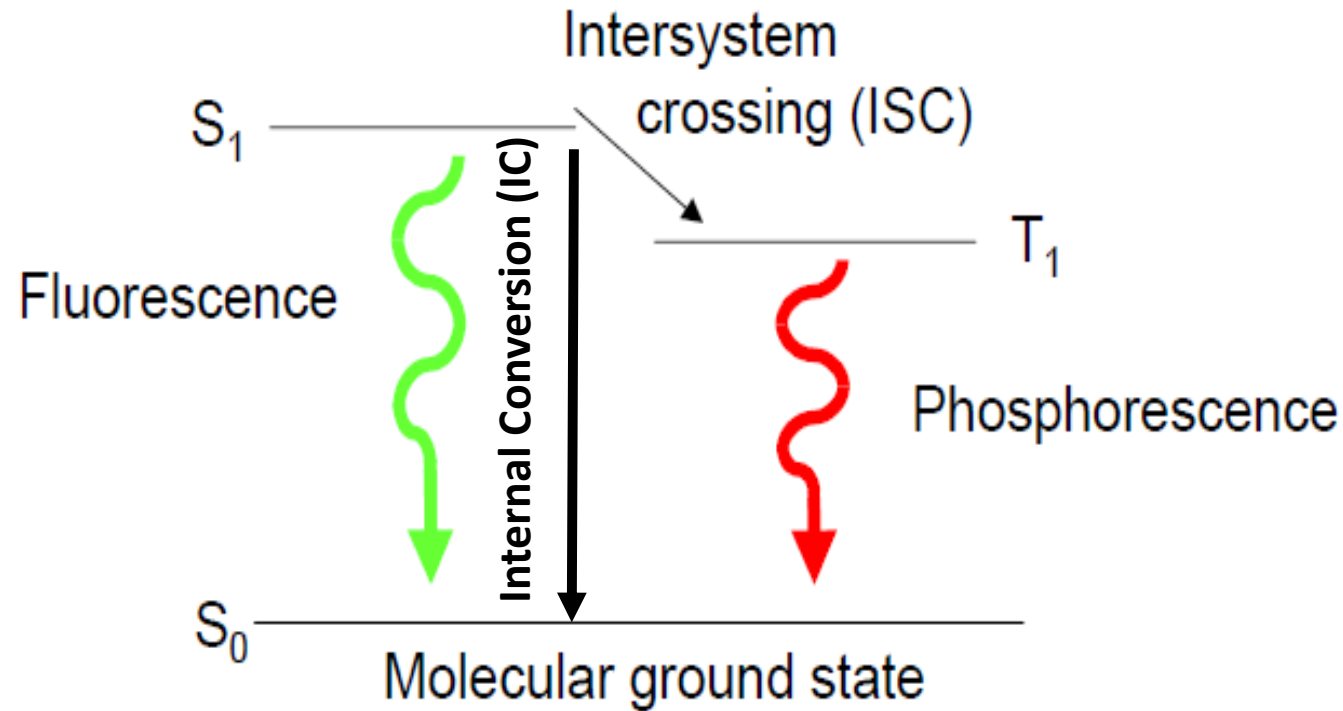
$$S = 2 \sum s_i + 1$$

Shows ground state and possible excited states

Triplets and singlets

- **Singlet lifetime \sim ns**
- **Triplet lifetimes \sim ms - secs**

Electronic Structure of Conjugated Systems-Simple Diagram!



Rate of disappearance = $K_F [S_1^*] + K_{IC} [S_1^*] + K_{ISC} [S_1^*]$

Rate of appearance of $S_1^* = I_a$

Rate of fluorescence: $K_F [S_1^*]$ (S_1 to $S_0 + h\nu$)

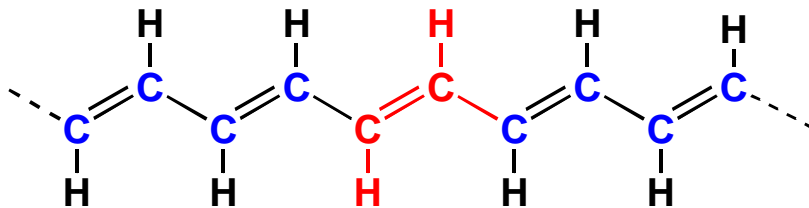
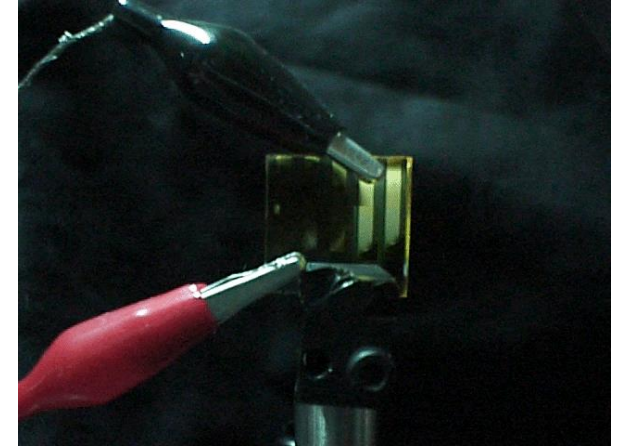
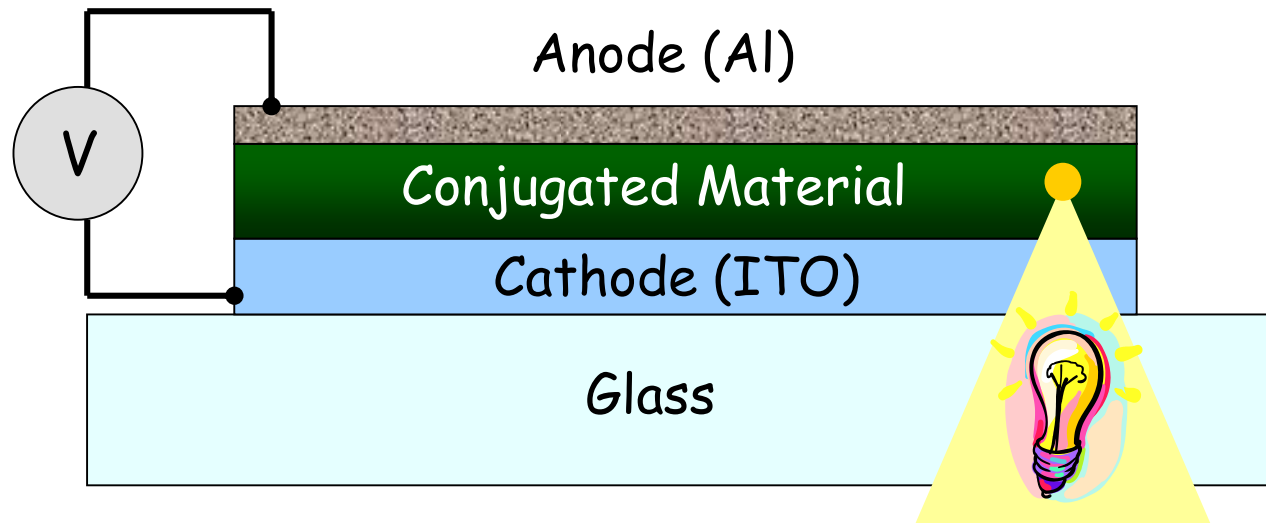
Rate of internal conversion: $K_{IC} [S_1^*]$ (S_1 to S_0)

Rate of intersystem crossing: $K_{ISC} [S_1^*]$ (S_1 to T_1)

Problems

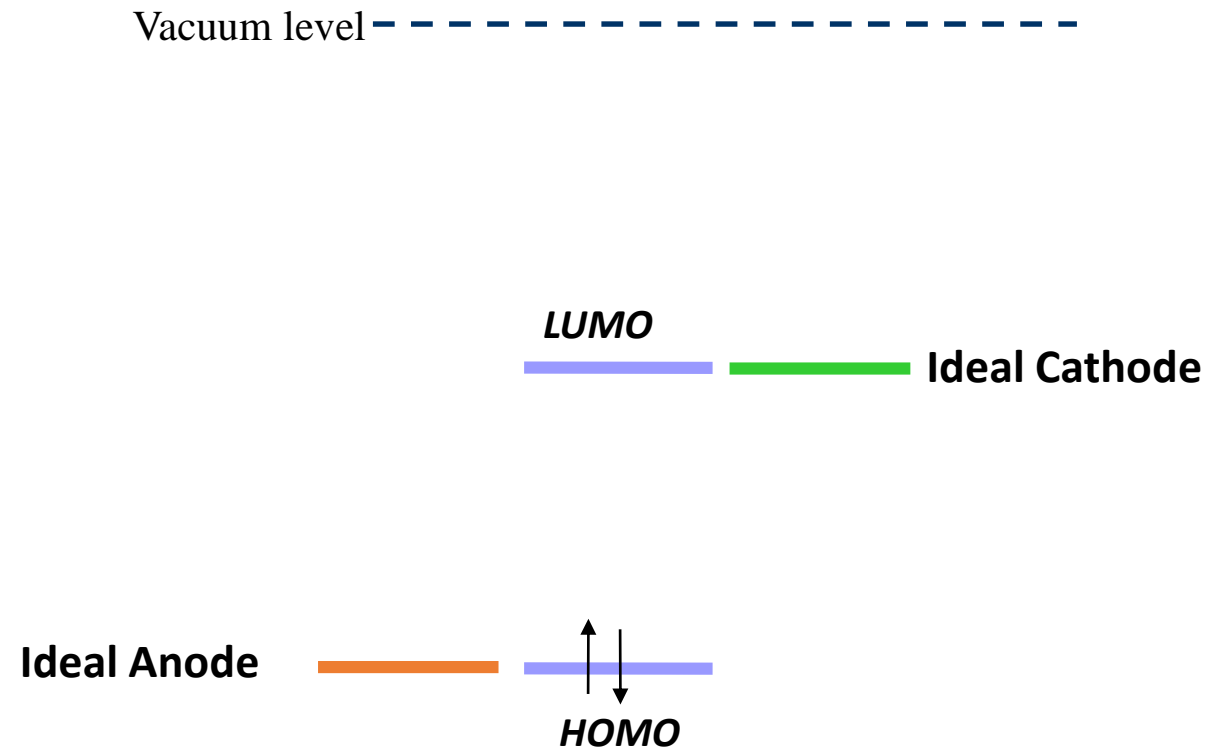
- Fluorescence quantum yield and observed lifetime of tryptophan in water are 0.2 and 2.6 ns. Calculate fluorescence life-time.
- If, fluorescence quantum yield=0.35 and fluorescence emission decayed with a half-life of 5.6 ns. Calculate fluorescence rate constant.

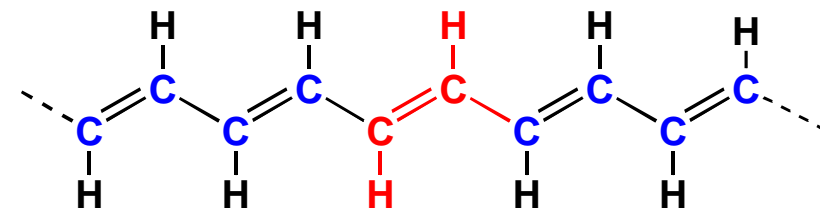
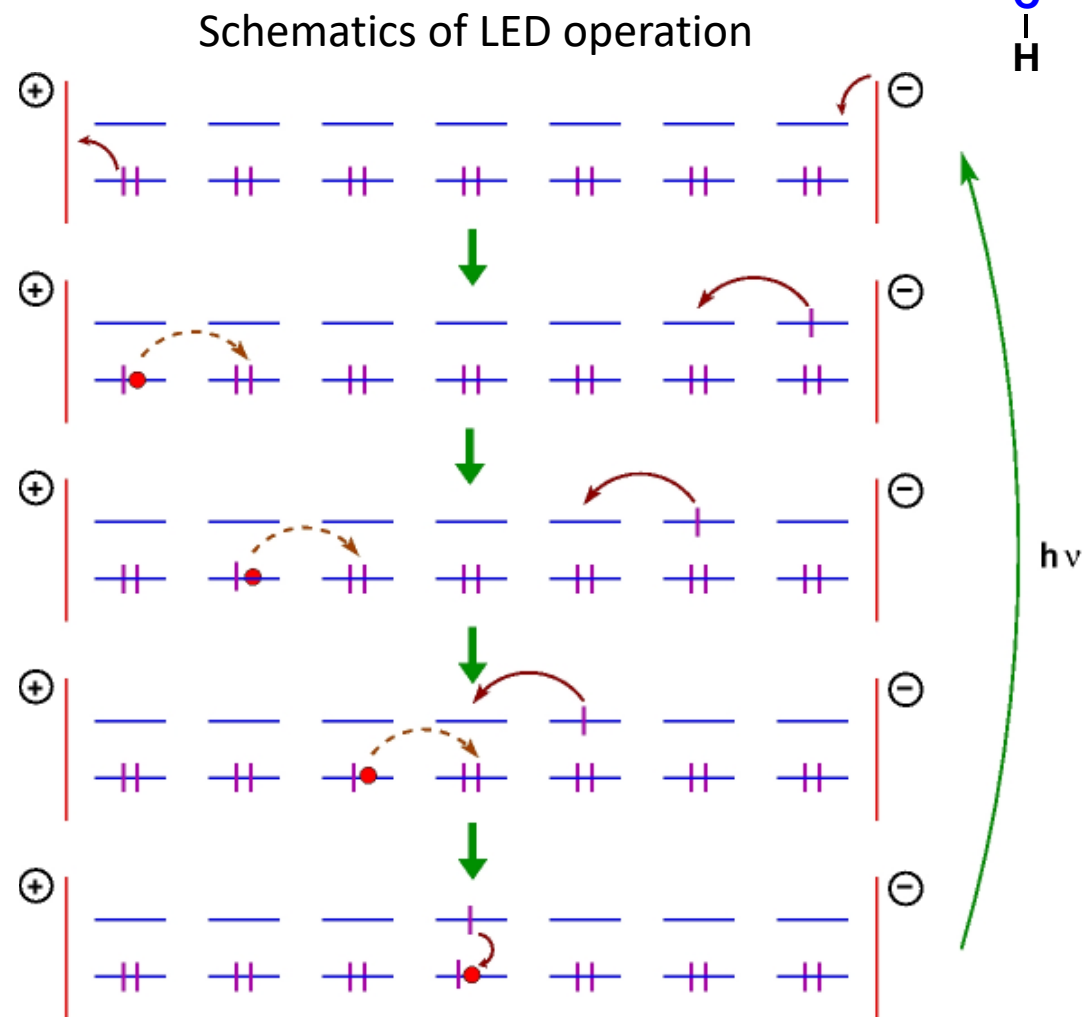
OLED



R.H. Friend *et al.*, Nature 397, 121 (1990)

CONTACT LAYERS

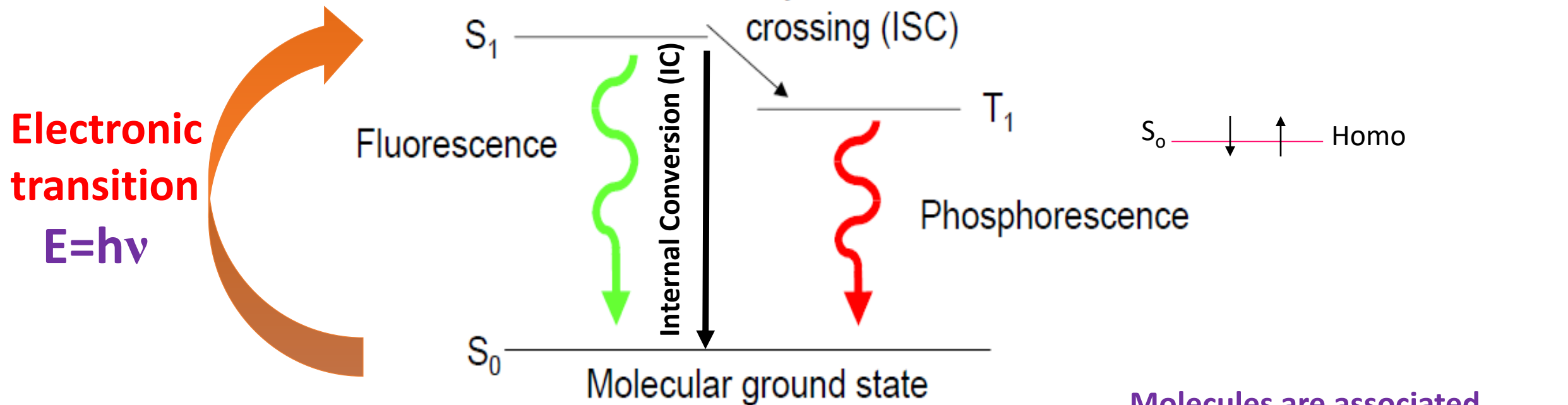




Electronic Structure of Conjugated Systems-Simple Diagram! (detail calculation in the next class)

4. Jablonski Diagram.

5. OLED in action.



Molecules are associated with vibrational levels!

***Simple Harmonic Oscillator
Vibrational Levels***

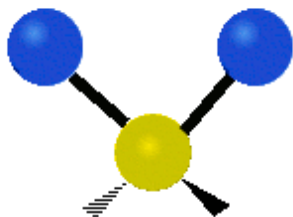
A molecule is associated with many 'vibrational levels'!

Table 4.1.1 Energy Difference between the Two Successive Energy Levels

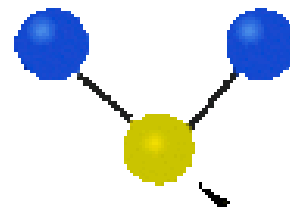
<i>Motion</i>	$\approx \Delta E/\text{J molecule}^{-1}$	$\approx \lambda/\text{m}$
Rotation	10^{-23}	10^{-2}
Vibration	10^{-21}	10^{-4}
Electronic	10^{-19}	10^{-6}

Details in the Next Class

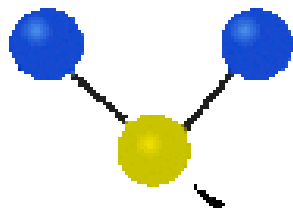
Molecular Vibrations



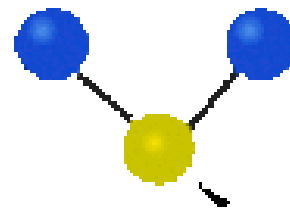
Symmetrical
stretching



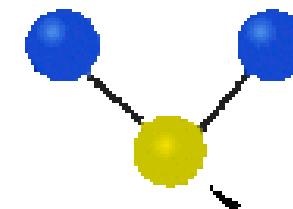
Rocking



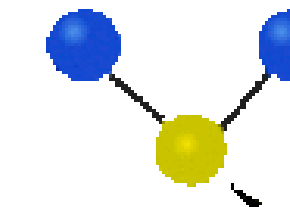
Asymmetrical
stretching



wagging



Scissoring



Twisting

Let us consider a particle of mass m is oscillating about its equilibrium position:

$$\text{Restoring force (F)} = -k_f x$$

(-ve sign indicates restoring force is acting in the opposite direction)

(k_f =force constant; x =displacement)

In classical mechanics, the above motion can be described in terms of Newton's law of motion:

$$F = mf = m \times d^2x/dt^2 = -k_f x \text{-----(1)}$$

Solution of eqn 1:

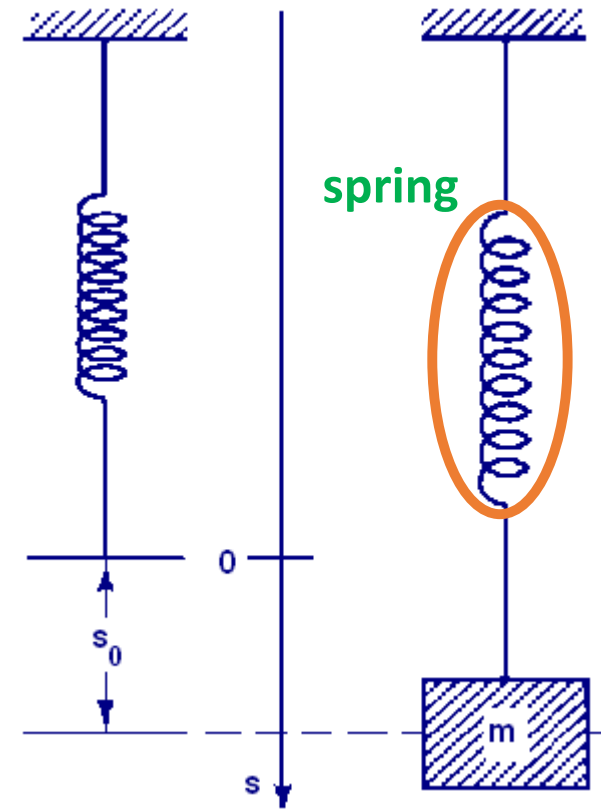
$$x = A \sin(2\pi v_0 t)$$

Or

$$x = A \cos(2\pi v_0 t)$$

Incorporating solution in eqn. 1, we get the following:

$$v_0 = 1/(2\pi) \times \sqrt{(k/m)} = \text{frequency of vibration}$$



Potential Energy [V]

Potential energy at any instance:

$$F = -dV/dx$$

$$dV = -Fdx$$

$$\int_0^v dV = K_f \int_0^x x dx$$

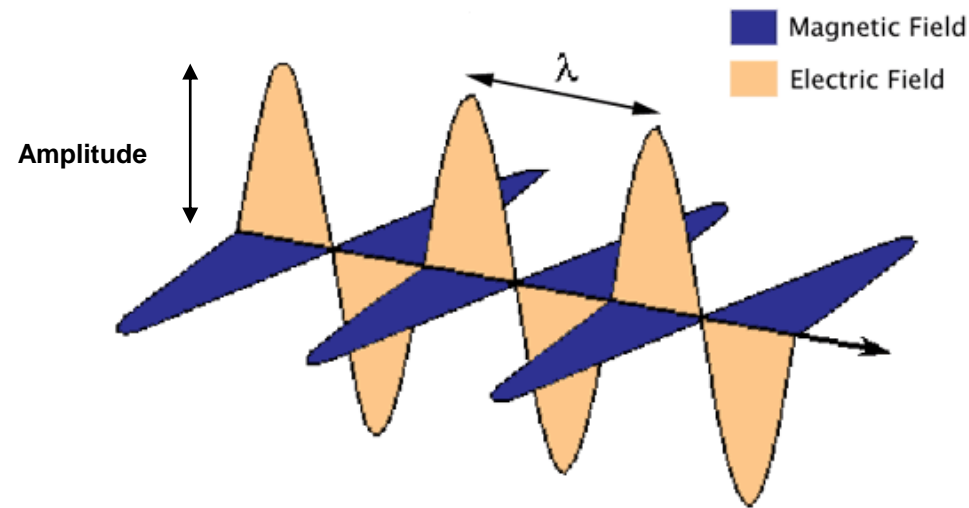
$$V = k_f(x^2/2)$$

Molecular Vibrations

$$\nu_0 = 1/(2\pi) \times \sqrt{(k/\mu)} = \text{frequency of vibration}$$

$$\mu = m_1 m_2 / (m_1 + m_2)$$

- In IR spectroscopy we are concerned with interaction between the oscillating electrical field of the wave and changing electrical fields resulting from vibration and rotational motion in the molecules in the sample
- Only those vibrational and rotational motions which result in an oscillating electrical dipole will be infrared active



Vibrational spectroscopy generates due to periodic molecular vibrations in materials

Analysis of IR spectra

3650 - 3200	O-H fundamental stretch alcohol and H ₂ O
(Blob peak)	O-H fundamental stretch of –COOH acids
3650 - 3200 (often doublet)	N-H fundamental stretch of amines (-NH ₂)
3350 (stronger) 3170 (weaker)	N-H fundamental stretch of amides (NH CO)
3150 – 3000	C-H fundamental stretch of aromatic rings
3150 – 3000	C-H fundamental stretch of vinyl
2960	Asymmetric –CH ₃ stretch
2870	Symmetric –CH ₃ stretch
2920	Asymmetric –CH ₂ stretch
2850	Symmetric –CH ₂ stretch
2240	C≡N
2270	-N=C=O (isocyanates)
2200 - 1700	C-H bonds of aromatic rings
1870 – 1540	C=O (carbonyl) (large dipole moment ⇒ strongest peak)
C=O summary	
1760 – 1700 1710 -1665 1650 - 1550	Aliphatic Aromatic Carboxylate anions Acids
1750 – 1735 1730 -1715 1770	Aliphatic Aromatic Vinyl esters (C=O directly attached to C=C) Esters
1690 – 1630 1570 -1515	Amide I Amide II (N-H and C-N combination) Amides
1720 – 1700 1690 - 1630 1570 - 1515	Ester C=O Amide I C=O Amide II Urethanes

1600	C=C of aromatic rings
1600	C=C of vinyl bonds
1500 – 1400	C-C in ring
Finger print region (fundamental + overtone)	
1450	Asymmetric –CH ₃ bend
1375	Symmetric –CH ₃ bend
1465	Asymmetric –CH ₂ scissoring
1350 - 1150	Symmetric –CH ₂ twist and wag
1310 – 1250	Aromatic ester (-C(O)O-C-)
1420 – 1160	Aliphatic ester (-C(O)O-C-)
1150 – 1085	C-O-C (ester and ether)
1085 – 1000	C-O-H (alcohol)
900 – 675	Fundamental out of plane C-H bending in ring
1000 - 675	Fundamental out of plane C-H bending in C=C
720	-CH ₂ rocking band
1415 - 1380	Organic sulfates Asymmetric S=O
1200 - 1185	Organic sulfates Symmetric S=O
1110 – 830	Si-O and Si-C
1260	C-H bend of Si-CH ₃

Time Independent Schrödinger Equation-SHO

$$\left[\frac{-\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x) \right] \psi = E \psi$$

$$V(x) = \left(\frac{1}{2}\right) K x^2$$

$$\left[\frac{-\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + \frac{1}{2} K x^2 \right] \psi = E \psi$$

$$E_v = (\nu + 1/2) h \nu_0 \quad [\nu = \text{quantum number}]$$