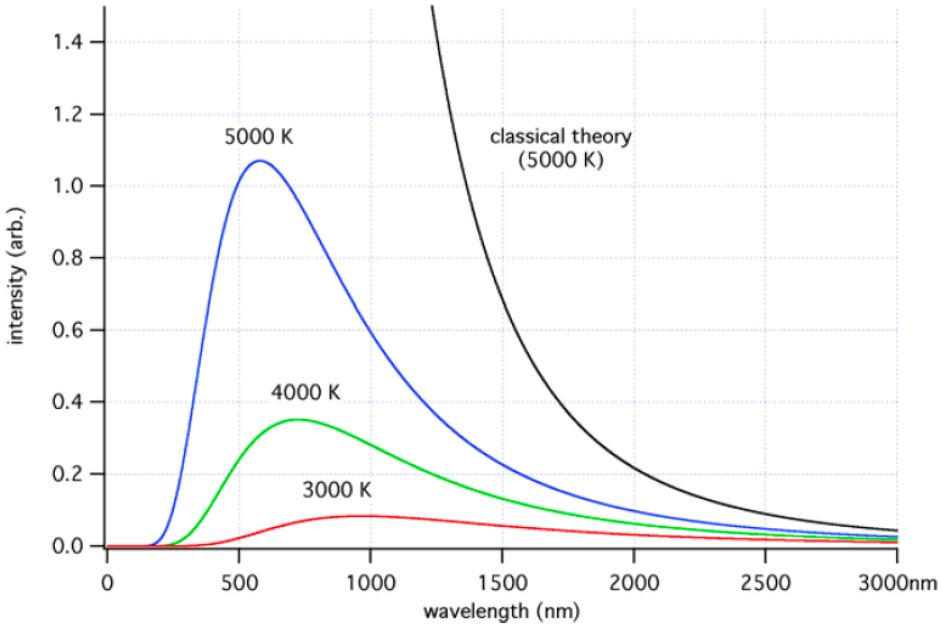
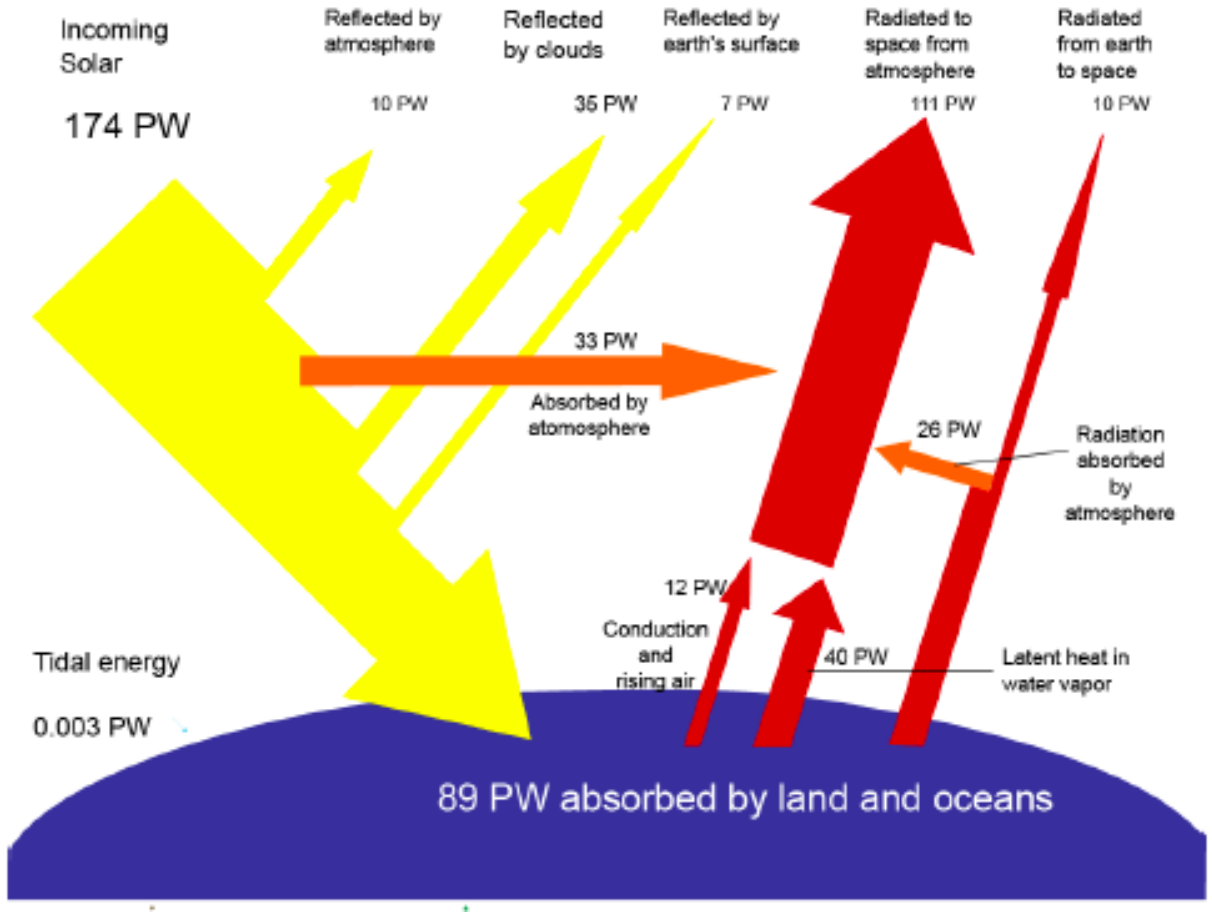
Recap



$$E(J) = h\nu = hc/\lambda$$

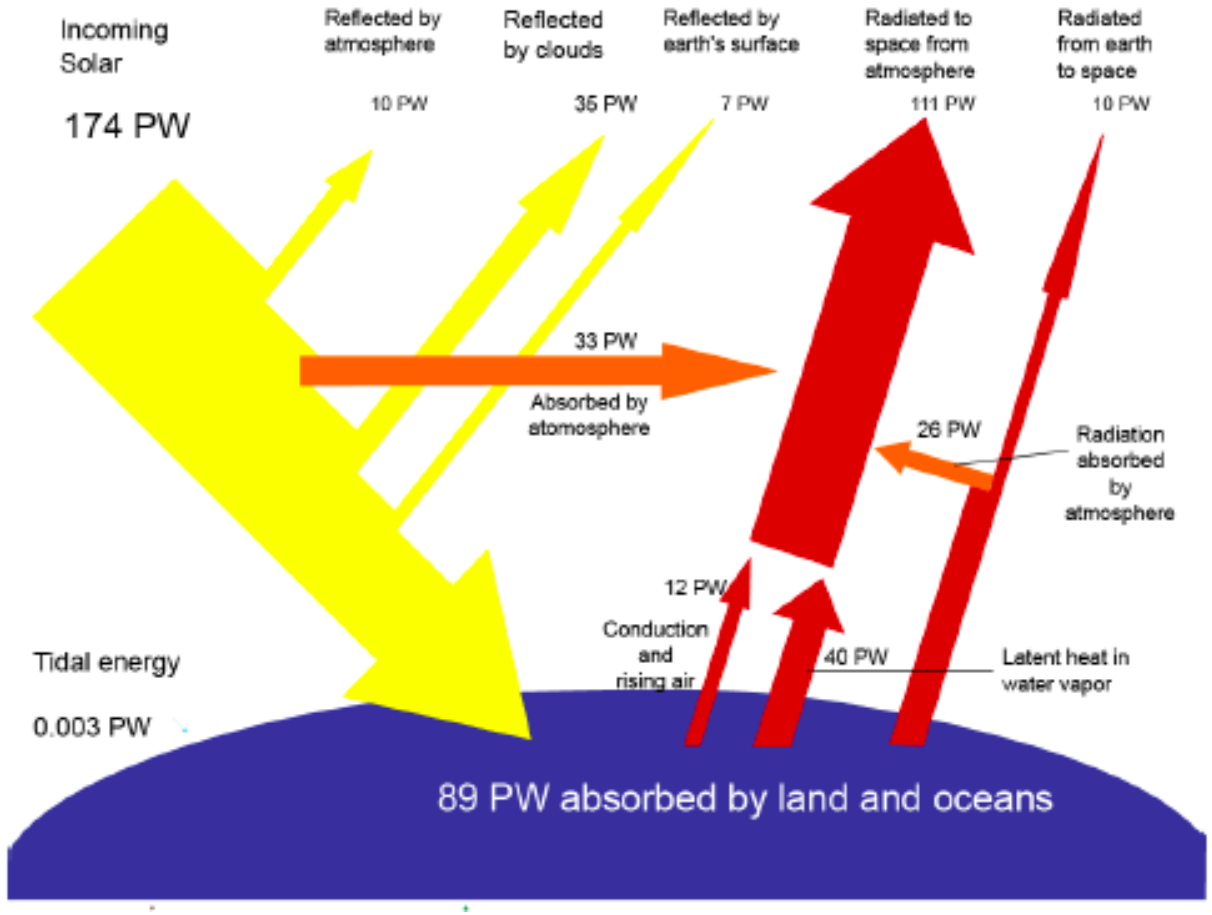
$$E(eV) = \frac{1240}{\lambda\,(nm)}$$



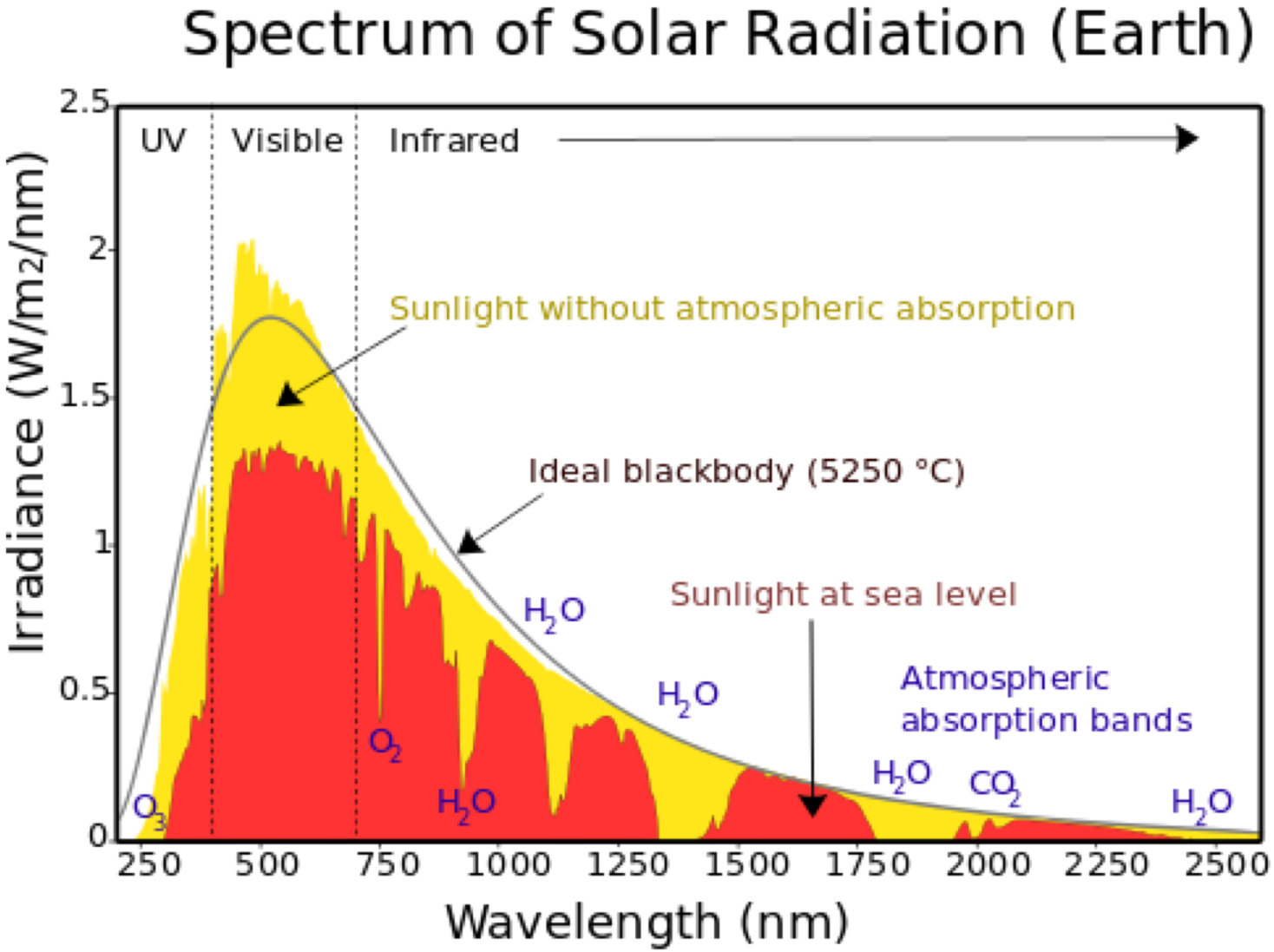
Recap

Atmospheric effect

- Absorption, scattering, reflection in the atmosphere.
- A reduction in the power of the solar radiation.
- A change in the spectral content.
- Diffuse component into the solar spectrum.
- Local variations (clouds, sun hours).



Recap


Spectrum of Solar Radiation (Earth)
Irradiance (W/m2/nm)
Wavelength (nm)
UV
Visible
Infrared
Sunlight without atmospheric absorption
Ideal blackbody (5250 °C)
Sunlight at sea level
Atmospheric absorption bands
O3
O2
H2O
H2O
H2O
H2O
CO2
H2O
2.5
2
1.5
1
0.5
0
250
500
750
1000
1250
1500
1750
2000
2250
2500

Solar Energy to The Earth

AM	Comments	Solar constant (W/cm^2)	$h\nu_{av}$	N_{ph} ($cm^{-2}sec^{-1}$)
0	Outside atmosphere	1367	1.48 eV (838 nm)	5.8×10^{17}
1	Sea level, sun at zenith	1040	1.32 eV (939 nm) **Red shift**	5.0×10^{17}
2	Sea level, sun at 60 degree from zenith	840	1.28 eV (969 nm) **Red shift**	4.3×10^{17}
3	Sea level, sun at 70.5 degree from zenith	750	1.21 eV (1025 nm) **Red shift**	3.9×10^{17}
1	Cloudy weather	120	1.44 eV (861 nm) **Blue shift**	5.2×10^{16}

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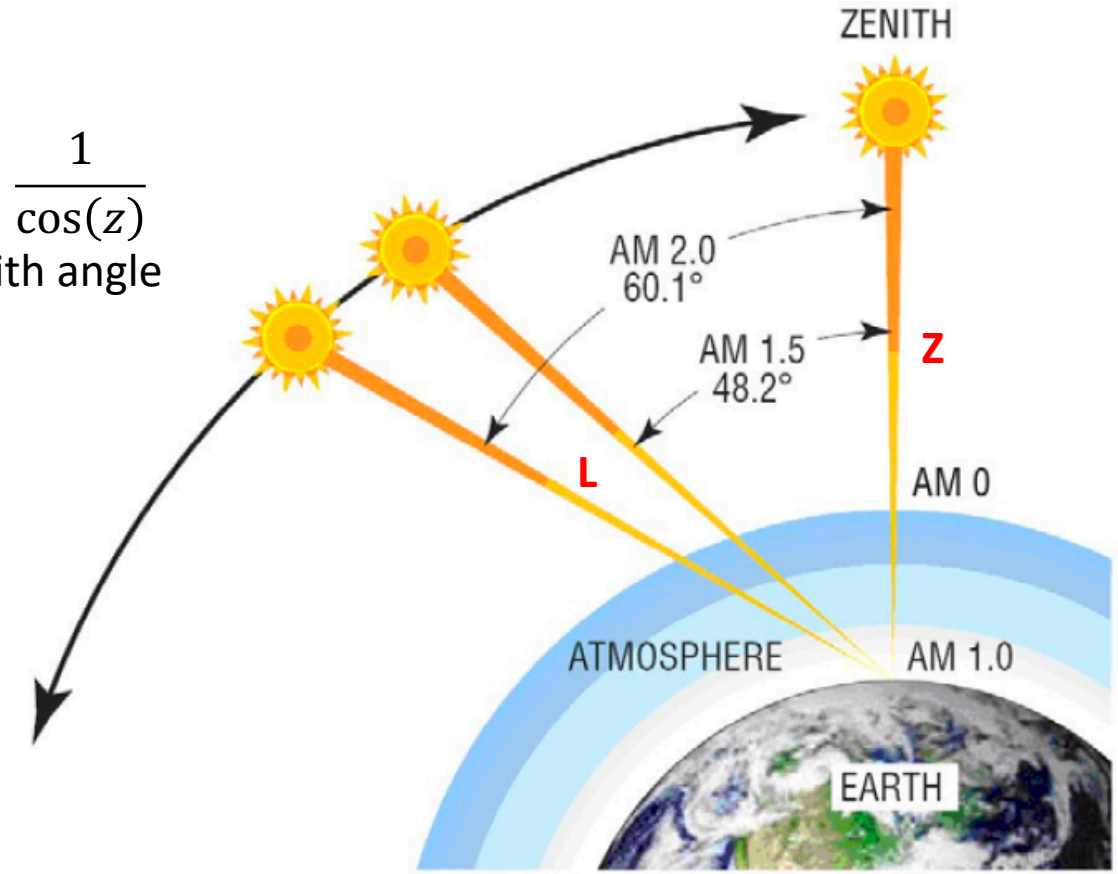
Air Mass

The Air Mass is the path length which light takes through the atmosphere normalized to the shortest possible path length that is, when the sun is directly overhead.
Hence, the Air Mass quantifies the reduction in the power of light as it passes through the atmosphere and is absorbed by air and dust.

$$AM \approx \frac{1}{\cos(z)}$$

Z = zenith angle



$$\cos z = \frac{Z}{L} = \frac{1}{AM}$$

Neglect the curvature of the earth!

Air Mass

$$AM \approx 1/\cos(z)$$

This is reasonably accurate for value of z up to around 75 degree.

$$AM = \sqrt{(r\cos(z))^2 + 2r + 1} - r\cos(z)$$

Modelling the atmosphere as a simple spherical shell provides a reasonable approximation(1)

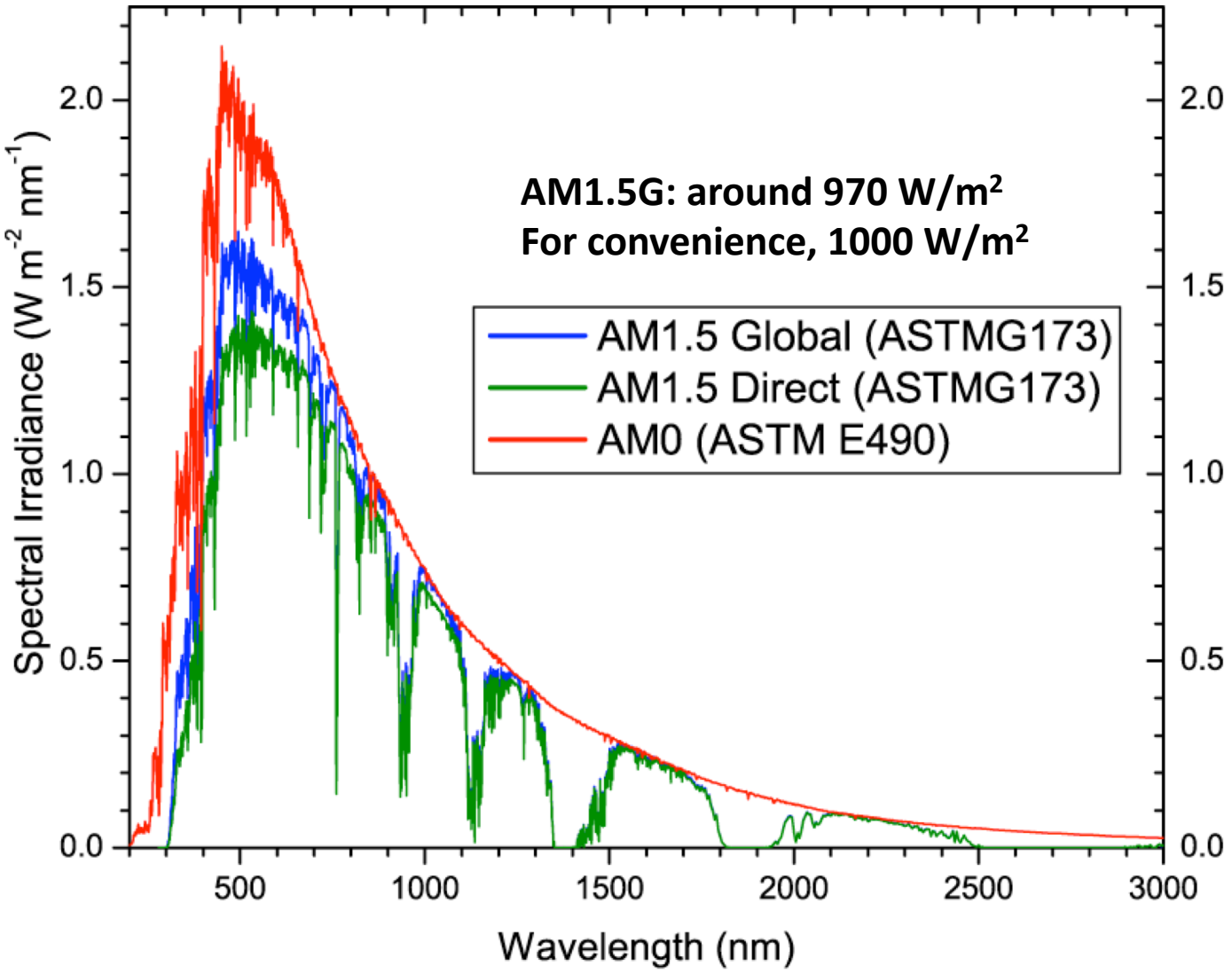
(1) Schoenberg, E. Theoretische Photometrie, g) Über die Extinktion des Lichtes in der Erdatmosphäre. In *Handbuch der Astrophysik*. Band II, erste Hälfte. Berlin: Springer (1929).

r = the radius of the Earth/the effective height of the atmosphere = 6371/9

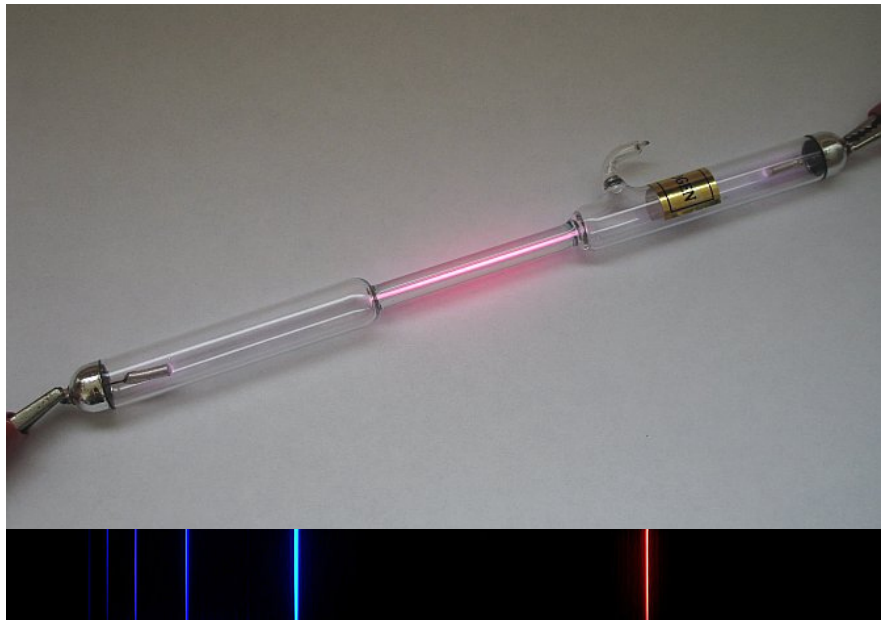
z (degree)	Flat Earth	Spherical shell	Global irradiance (W/m^2)
0	1.0	1.0	1367
48.2 60	1.5 2.0	2.0	840
70	2.9	2.9	710
75	3.9	3.8	620
80	5.8	5.6	470
85	11.5	10.6	254
88	28.7	20.3	96
90	∞	37.6	20

Standard Solar Spectrum

- **AM Global = AM Direct + AM Diffuse**

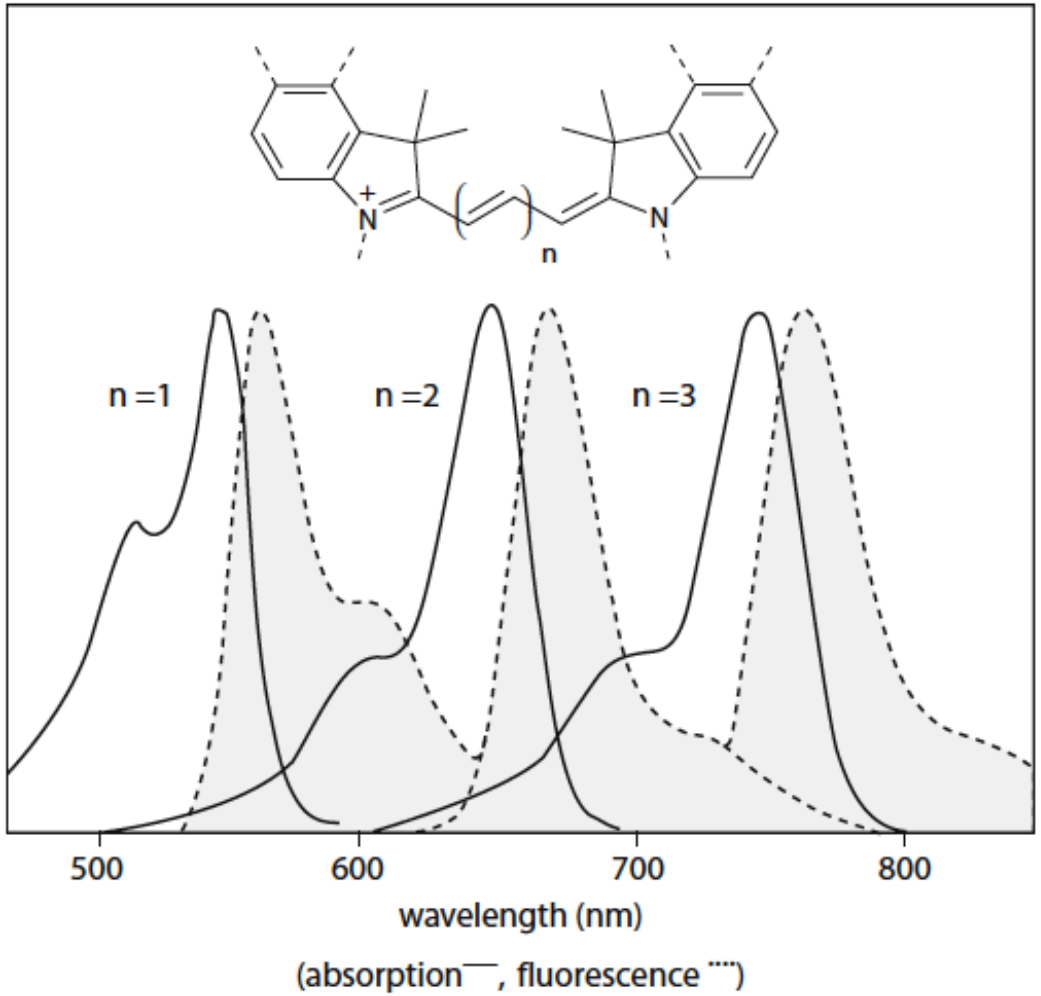


Spectra in Many Atoms

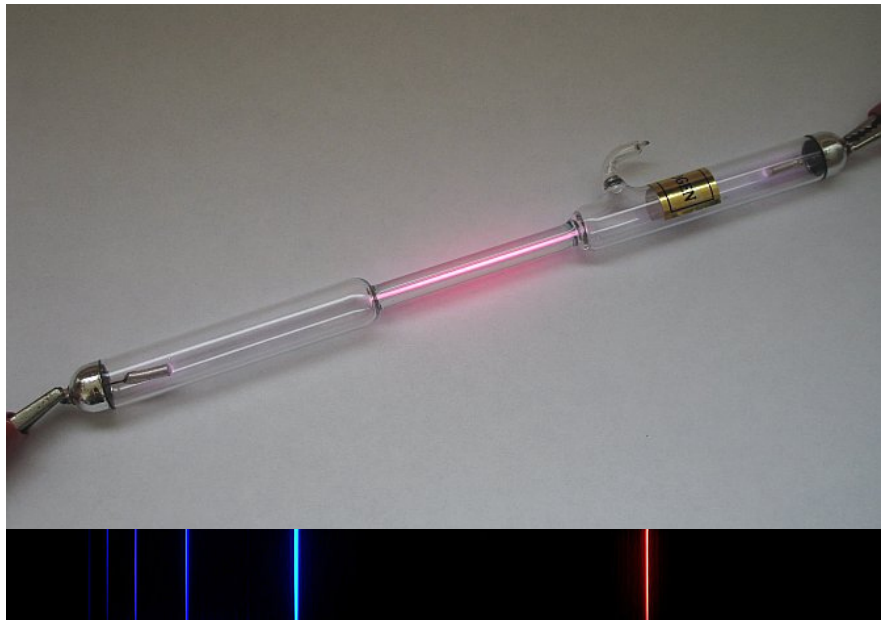


Emission by Hydrogen

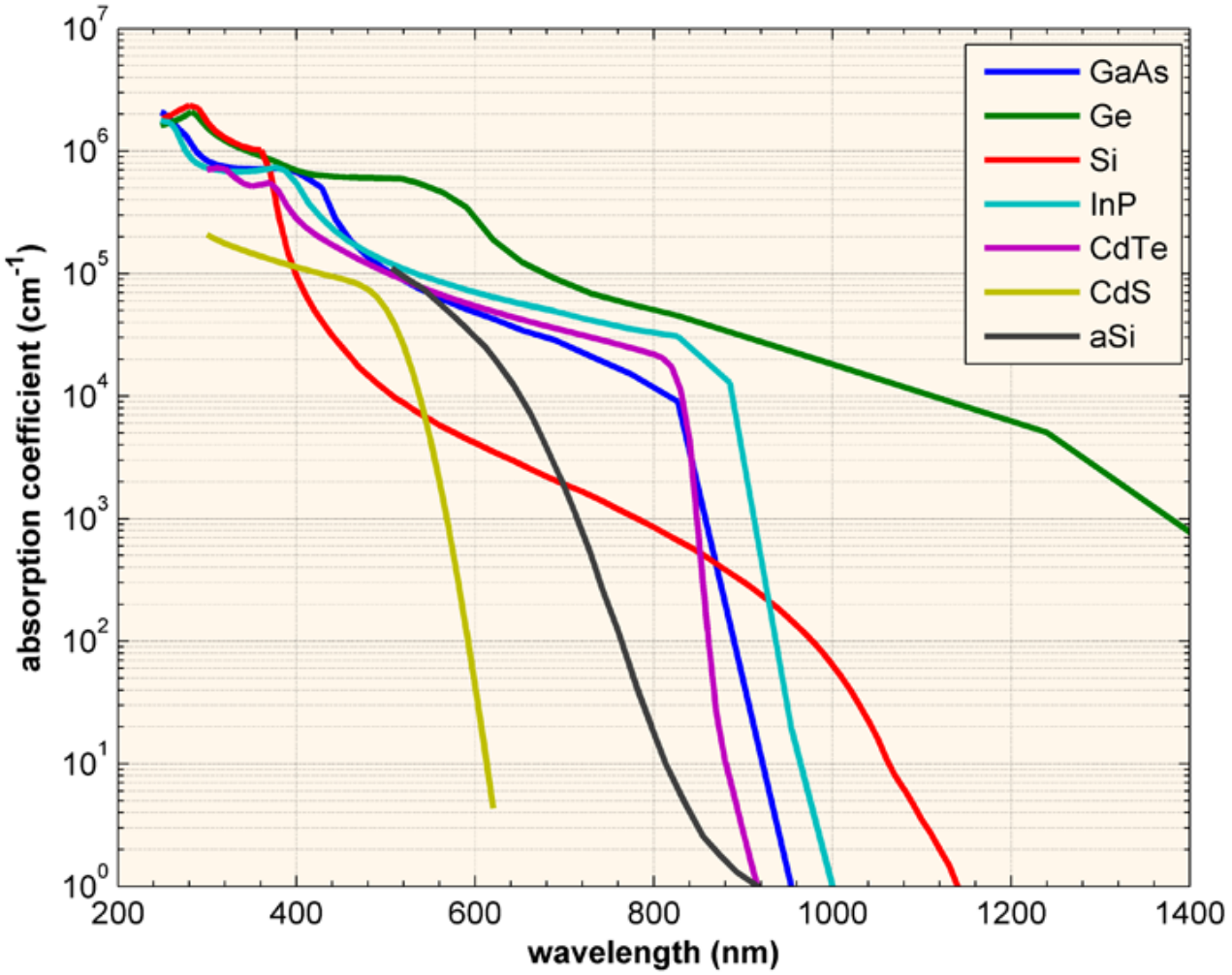
Cyanine dyes



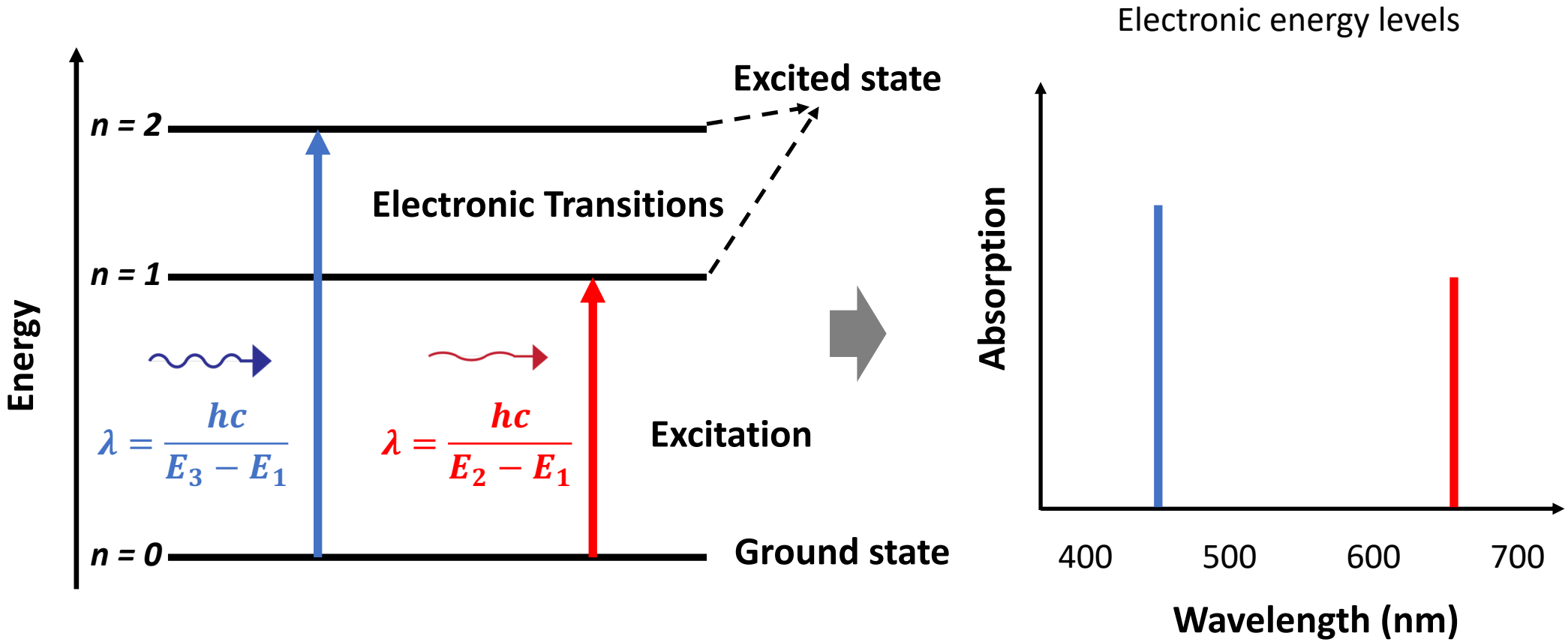
Spectra in Many Atoms



Emission by Hydrogen

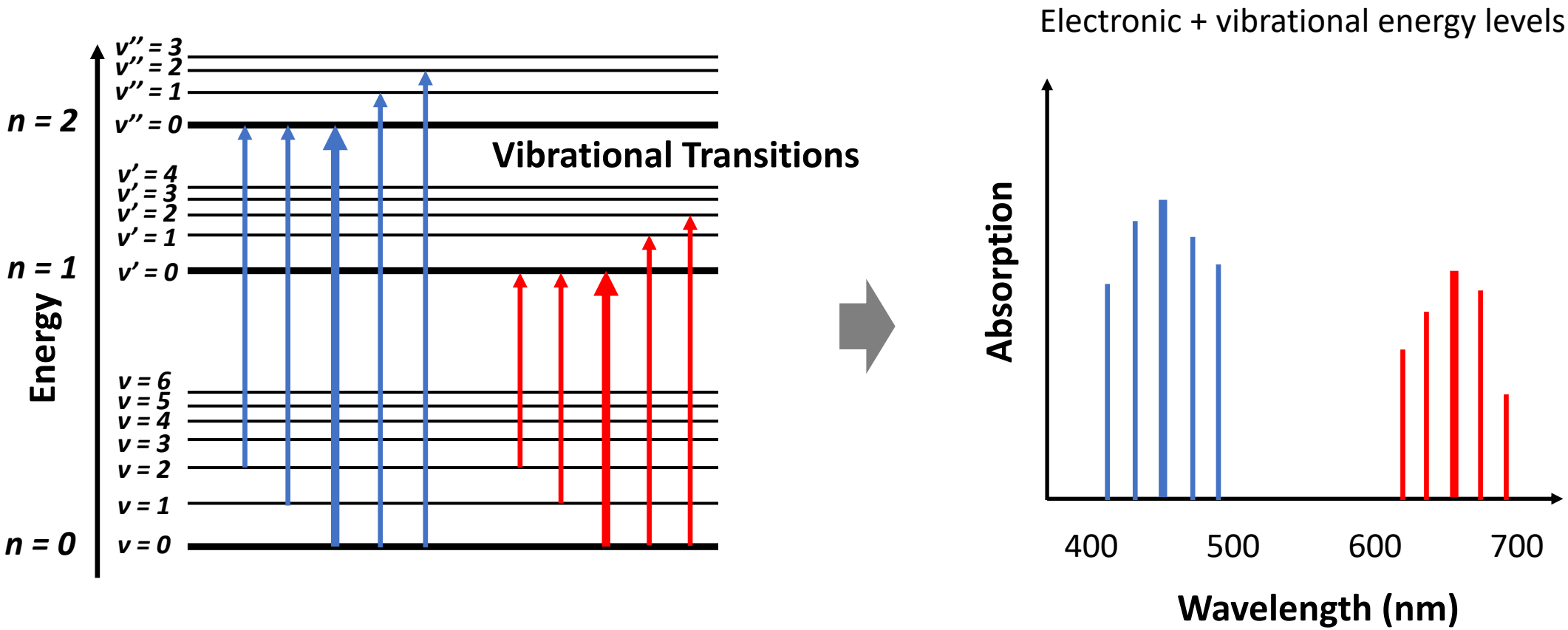


Physics in Light Absorption



- The probabilities for photon absorption are generally different for different transitions.
- In addition to the electronic energy levels, molecules also have vibrational modes. https://en.wikipedia.org/wiki/Molecular_vibration
- The spacing between the quantized vibrational energy levels is smaller than that of the electronic energy levels.

Physics in Light Absorption



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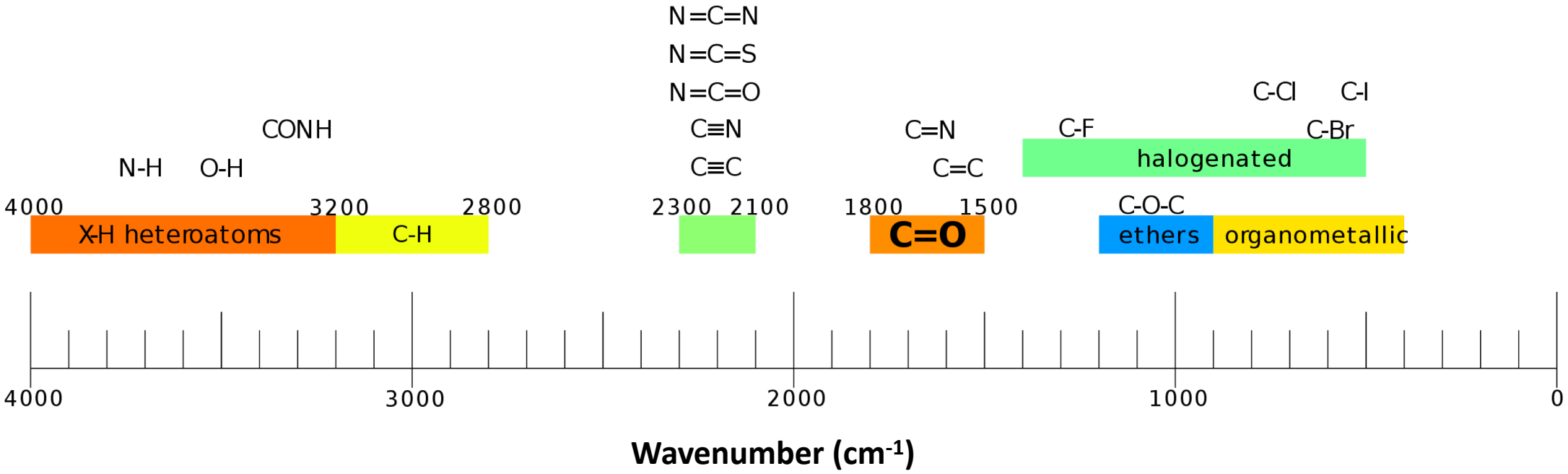
Physics in Light Absorption

List of main IR spectroscopy bands.

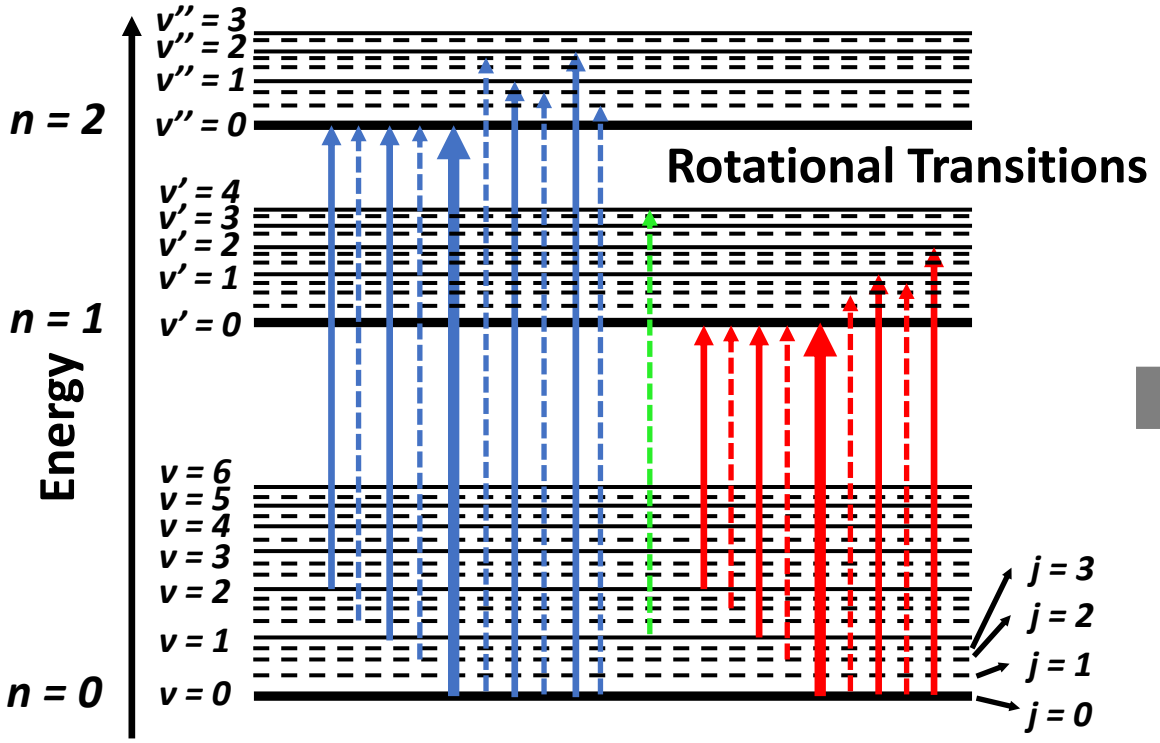


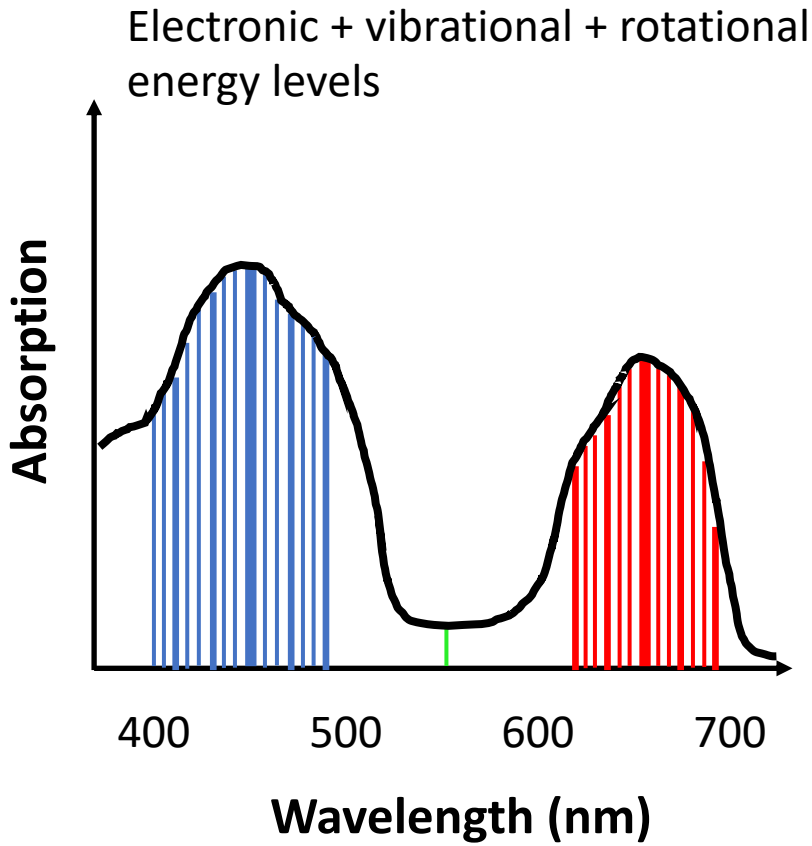
- Wavenumber (k) = wavelengths per unit distance = 1 / λ

$$E = h\nu = \frac{hc}{\lambda} = hck = 4.1357 \times 10^{-15}(eV \cdot s) \times 2.998 \times 10^{10}\left(\frac{cm}{s}\right) \times k = 0.000123984\ (eV \cdot s) \times k\ (cm^{-1})$$

- A wave with a wavenumber of k = 8065.544 cm^{-1} will have a photon energy of 1 eV.
- Vibrational energy states are on **the order of 1000 cm^{-1} (0.04 ~ 0.5 eV)**.

Physics in Light Absorption





- The entire molecule can rotate about an axis with some frequency, which are also quantized.
- Transition in the rotational mode requires very little energy (10^{-3} to 10^{-6} eV), so that microwave radiation (λ in millimeter to meter range) is adequate.
- The corresponding changes in absorption line wavelengths are in the sub-nanometer range, compared to electronic or electronic-vibrational transitions.

Ways to Dissipate The Energy from The Excited Electron

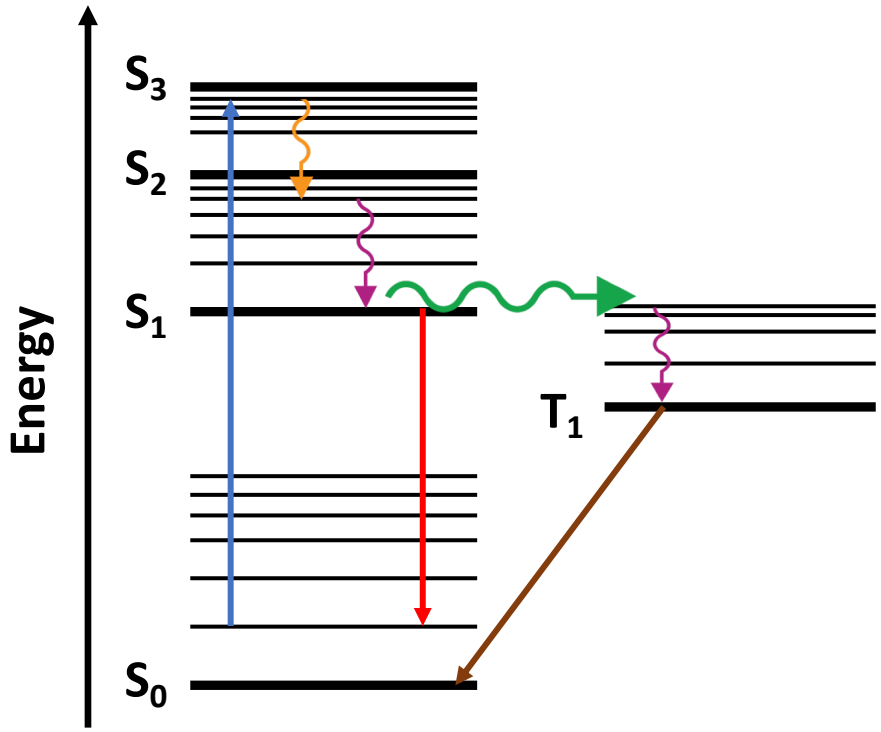
- **Internal Conversion**: The excited electron can transition from a vibration level in one electronic state to another vibration level in a lower electronic state, if vibrational energy levels strongly overlap electronic energy levels. As energies increase, the manifold of vibrational and electronic eigenstates becomes closer distributed.

- **Vibrational Relaxation**: The energy deposited by the photon into electron is given away to other vibrational modes as kinetic energy.

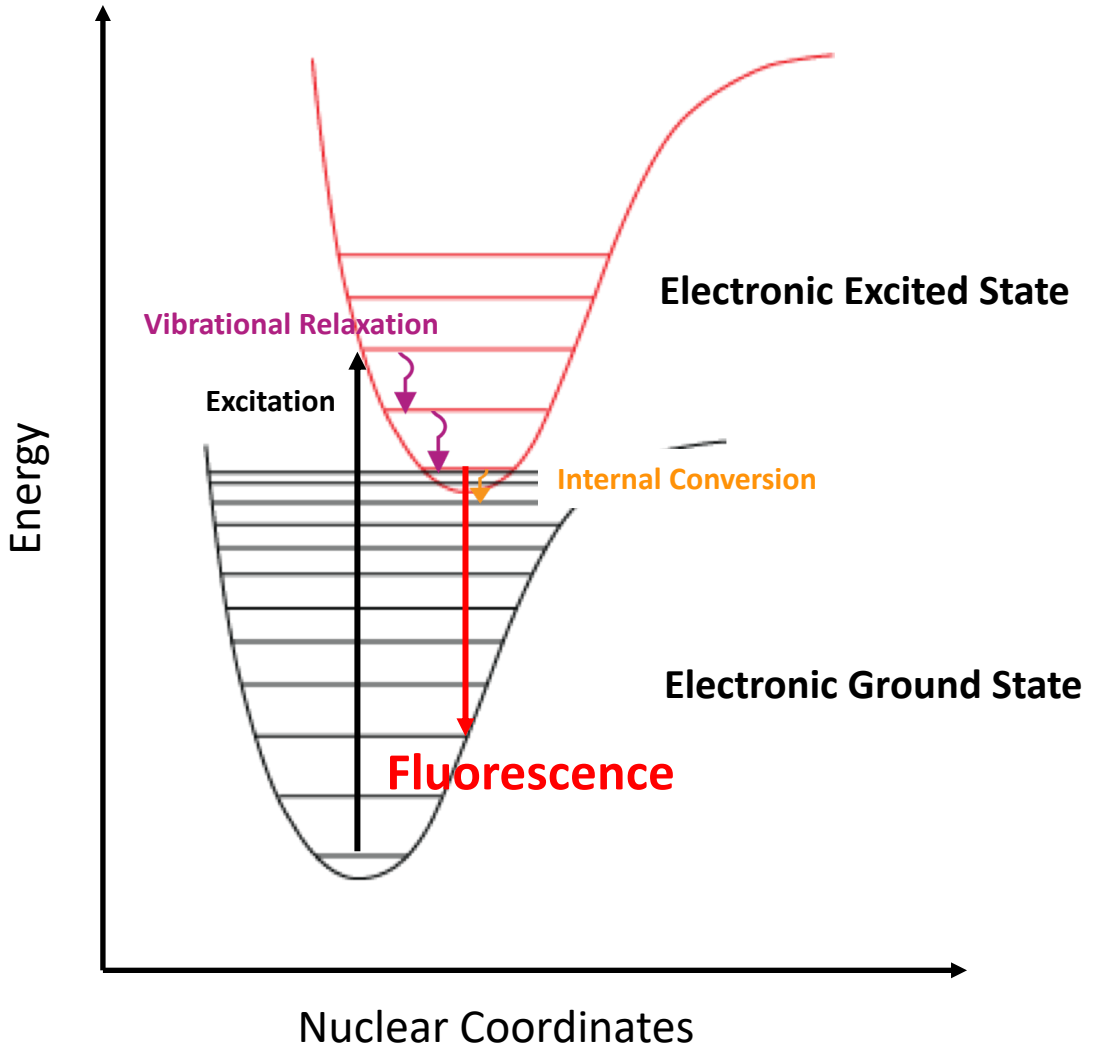
- **Fluorescence**: The vibrationally relaxed excited state returns to the ground state with emission of radiation.

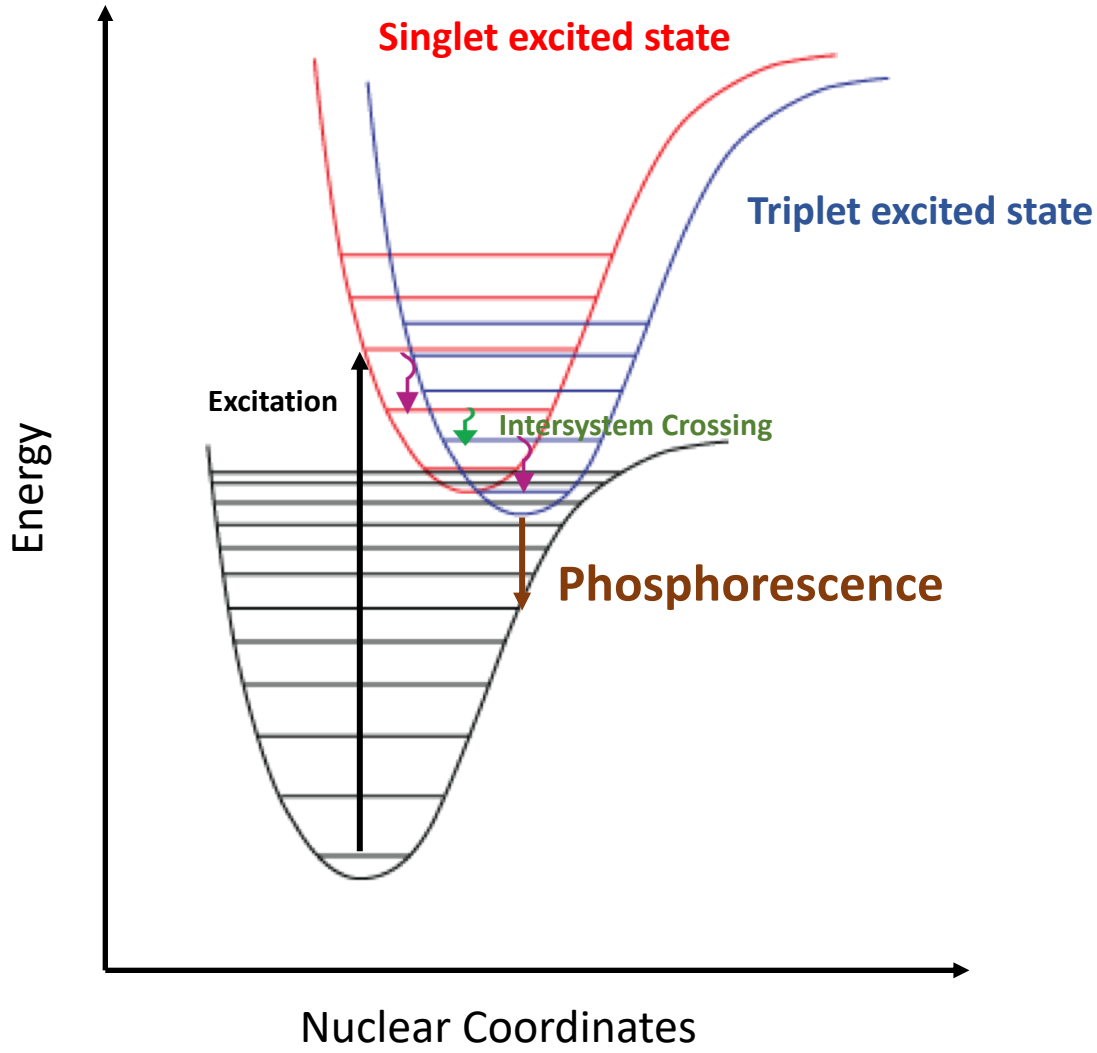
- **Intersystem Crossing**: The electron changes spin multiplicity from an excited singlet state to an excited triplet state.

- **Phosphorescence**: No direct access to the T1 state (spin selection rule). The way back to the ground state by emitting a photon a long time.

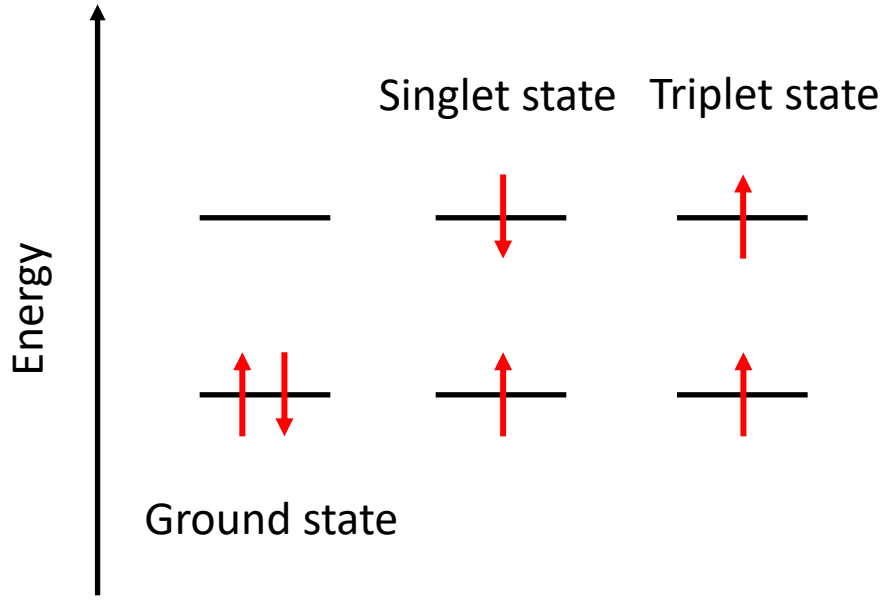


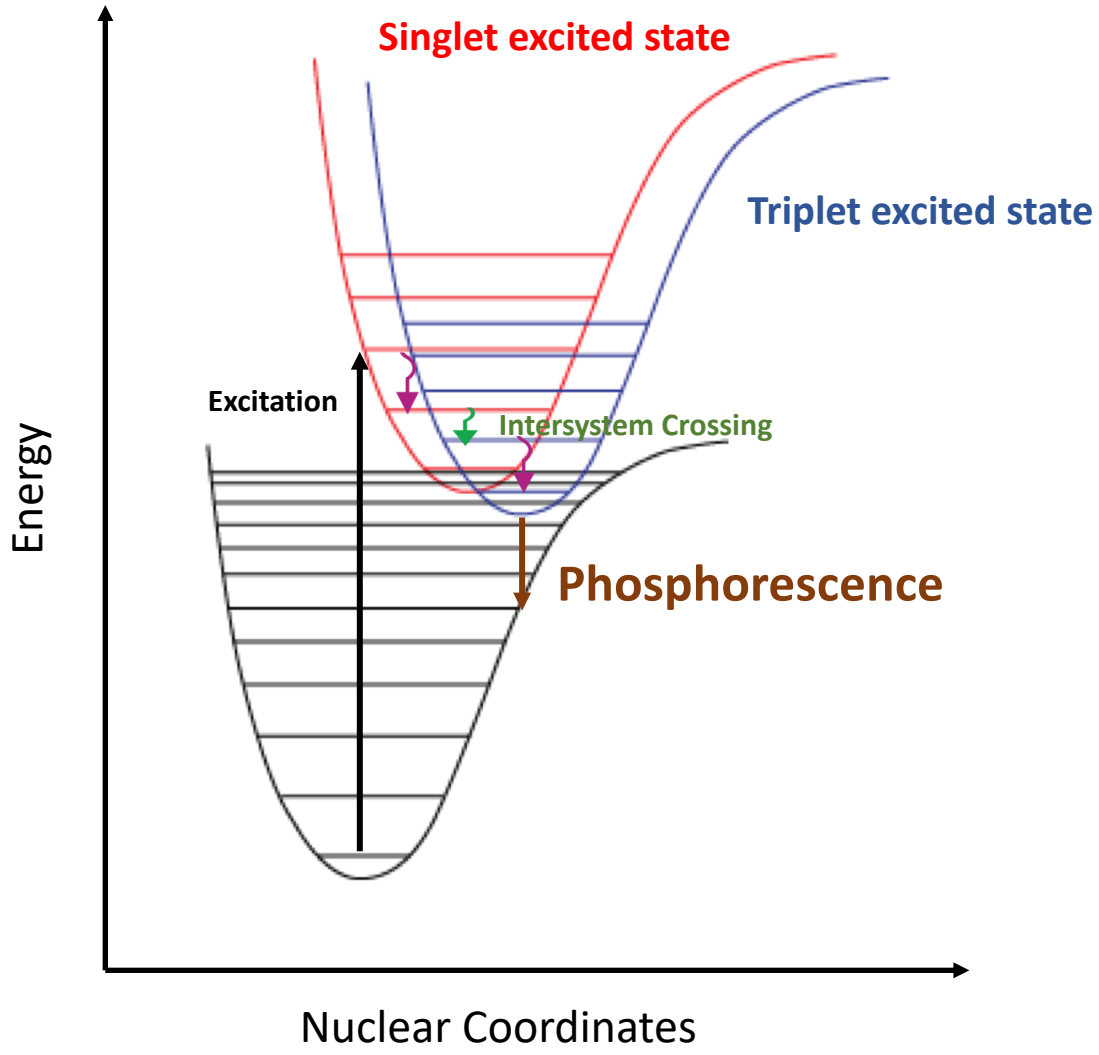
Ways to Dissipate The Energy from The Excited Electron



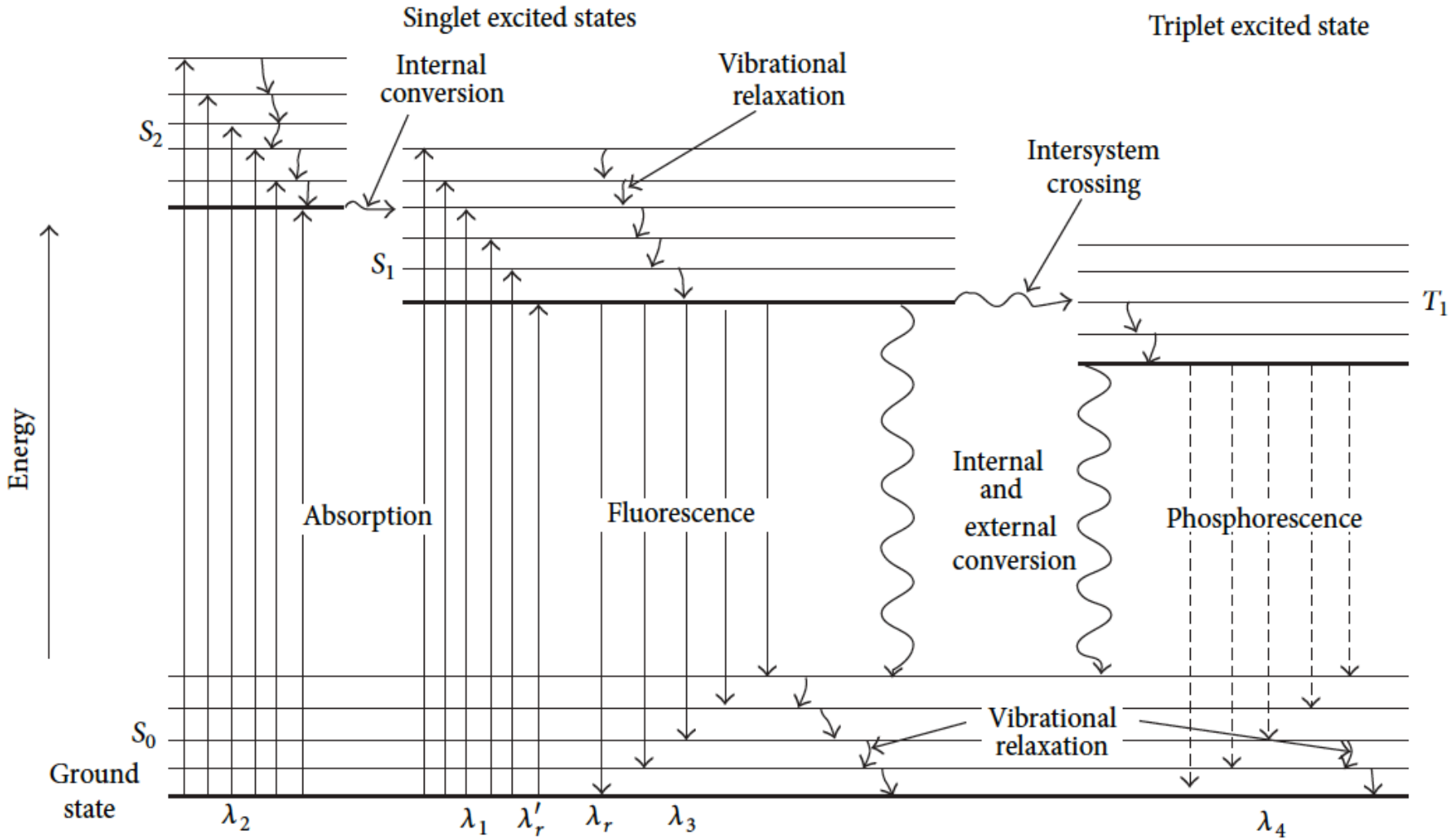


Ways to Dissipate The Energy from The Excited Electron





Fluorescence and Phosphorescence



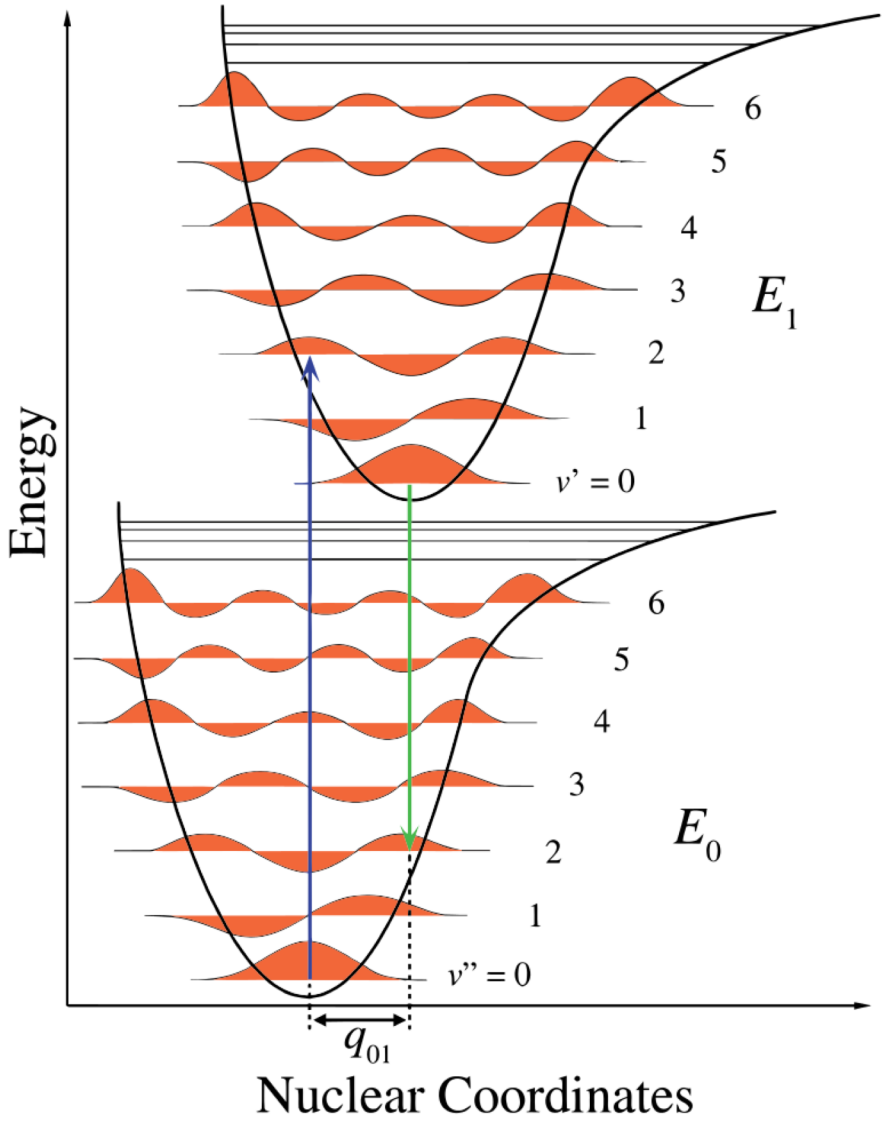
Jablonski diagram

T. H. Fereja et al., *ISRN Spectroscopy*, 2013, 12 (2013).

Timescale of Transitions

Transition	Time scale	Radiative process?
Absorption	10^{-15} sec	Yes
Internal Conversion	10^{-14} to 10^{-11} sec	No
Vibrational Relaxation	10^{-14} to 10^{-11} sec	No
Fluorescence	10^{-9} to 10^{-7} sec	Yes
Intersystem Crossing	10^{-8} to 10^{-3} sec	No
Phosphorescence	10^{-4} to 10^{-1} sec	Yes

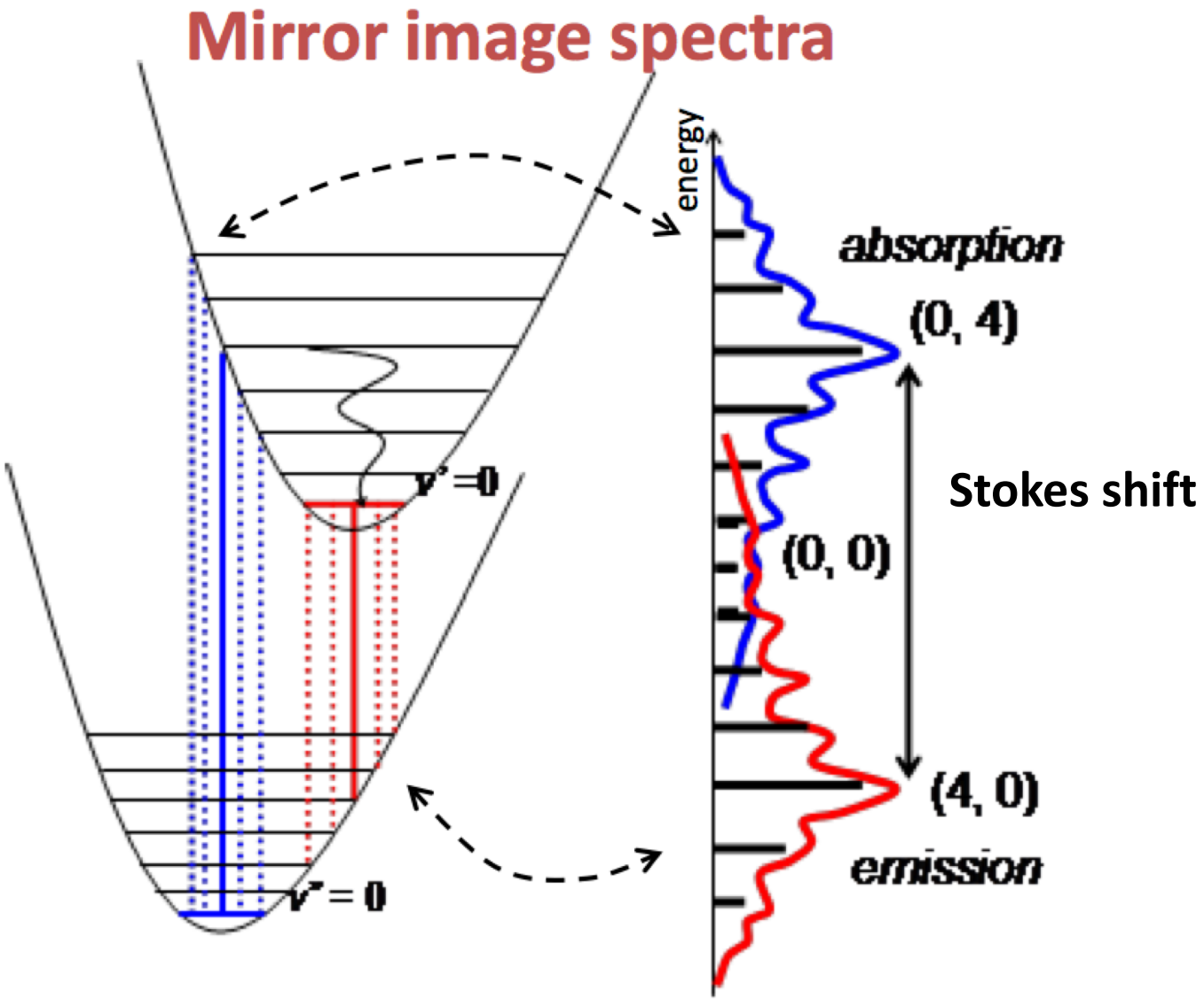
The Franck-Condon Principle



- The ground state and the excited states of molecules can be represented by harmonic oscillators with quantized vibrational modes.
- The nuclei are much more massive than electrons. Therefore, the electronic transition occurs in a stationary nuclear framework (**Franck-Condon Principle**).
- Electronic transition as vertical lines represents the same nuclear distribution in the ground and the excited states.
- The intensity of a vibrational transition is proportional to the square of the overlap integral between the vibrational wavefunctions of the two states that are involved in the transition.

$$P_{i\to f} = \left|\langle \psi^*_{final} | \mu | \psi_{initial} \rangle\right|^2 = \left| \int \psi^*_{final} \mu \psi_{initial} d\tau \right|^2$$

Absorption and Emission (Mirror Image Rule)



Stokes shift

1. The energy associated with emission transitions is typically less than that of absorption.

2. Fluorescence emission is usually accompanied by transitions to higher vibrational energy levels of the ground state.

3. Other events such as solvent orientation effects, excited-state reactions, complex formation, and resonance energy transfer can also contribute to longer emission wavelengths.