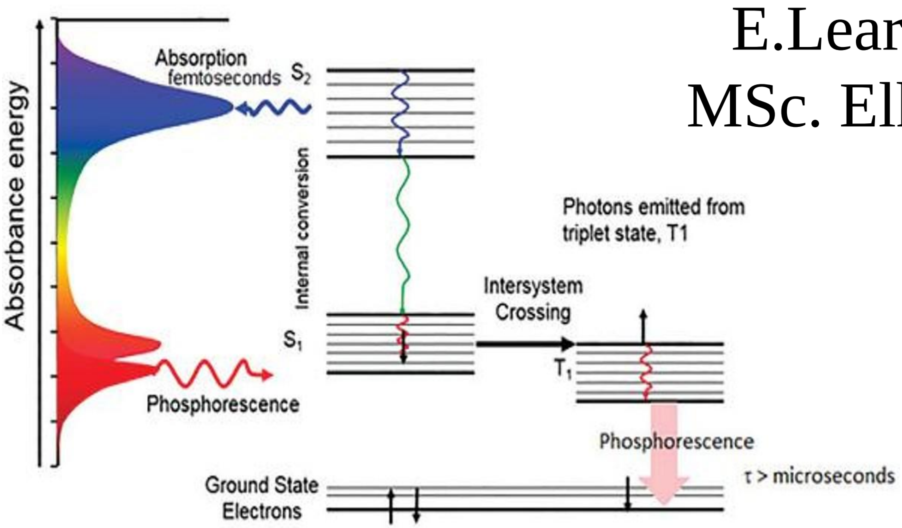
**Ministry of higher education and scientific research**
**AL-Mustaqbal University college**
**Department of medical physics**

**Analytical chemistry**

**Lecture 10**

# Fluorescence and phosphorescence spectrophotometric analysis




E.Learning by :
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# Introduction

- Fluorescence and phosphorescence are types of molecular luminescence methods.
- A molecule of analyte absorbs a photon and excites a species. The emission spectrum can provide qualitative and quantitative analysis.
- The term fluorescence and phosphorescence are usually referred as photoluminescence because both are alike in excitation brought by absorption of a photon.
- Fluorescence differs from phosphorescence in that the electronic energy transition that is responsible for fluorescence does not change in electron spin, which results in short-live electrons (<10-5 s) in the excited state of fluorescence.
- In phosphorescence, there is a change in electron spin, which results in a longer lifetime of the excited state (second to minutes). Fluorescence and phosphorescence occurs at longer wavelength than the excitation radiation..

- Fluorescence can occur in gaseous, liquid, and solid chemical systems.
- The simple kind of fluorescence is by dilute atomic vapors. A fluorescence example would be if a 3s electron of a vaporized sodium atom is excited to the 3p state by absorption of a radiation at wavelength 589.6 and 589.0 nm.
- After 10-8 s, the electron returns to ground state and on its return it emits radiation of the two wavelengths in all directions.
- This type of fluorescence in which the absorbed radiation is remitted without a change in frequency is known as resonance fluorescence.
- Resonance fluorescence can also occur in molecular species. Molecular fluorescence band centers at wavelengths longer than resonance lines. The shift toward longer wavelength is referred to as the Stokes Shift.

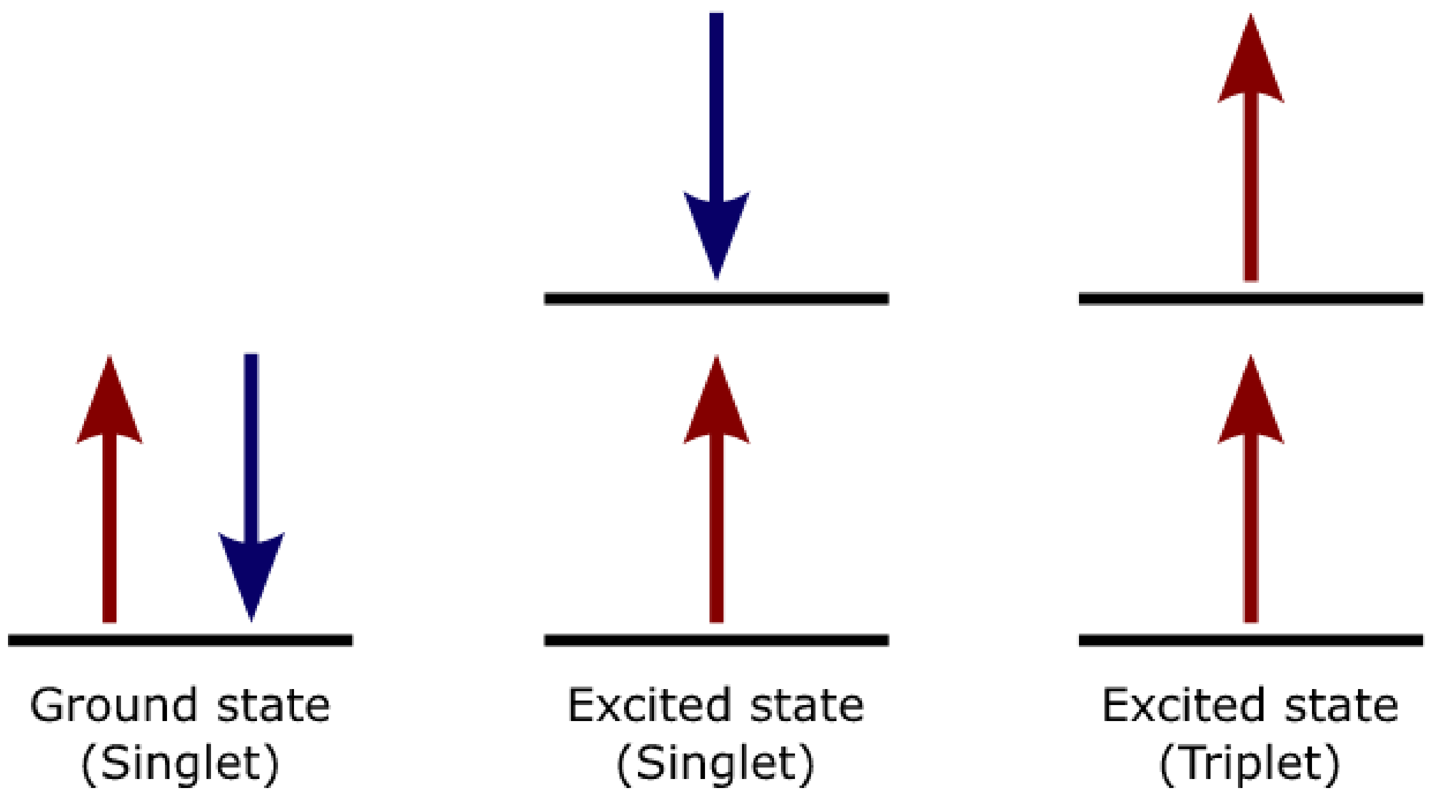
# Singlet and Triplet Excited State

- Understanding the difference between fluorescence and phosphorescence requires the knowledge of electron spin and the differences between singlet and triplet states.
- The Pauli Exclusion principle states that two electrons in an atom cannot have the same four quantum numbers ( n , l , ml , ms ) and only two electrons can occupy each orbital where they must have opposite spin states.
- These opposite spin states are called spin pairing. Because of this spin pairing, most molecules do not exhibit a magnetic field and are diamagnetic.
- In diamagnetic molecules, electrons are not attracted or repelled by the static electric field. Free radicals are paramagnetic because they contain unpaired electrons have magnetic moments that are attracted to the magnetic field.

## Singlet and Triplet Excited State

- Singlet state is defined when all the electron spins are paired in the molecular electronic state and the electronic energy levels do not split when the molecule is exposed into a magnetic field.
- A doublet state occurs when there is an unpaired electron that gives two possible orientations when exposed in a magnetic field and imparts different energy to the system.
- A singlet or a triplet can form when one electron is excited to a higher energy level. In an excited singlet state, the electron is promoted in the same spin orientation as it was in the ground state (paired).
- In a triplet excited stated, the electron that is promoted has the same spin orientation (parallel) to the other unpaired electron.

# The difference between the spins of ground singlet, excited singlet, and excited triplet



# Singlet and Triplet Excited State

- Singlet, doublet and triplet is derived using the equation for multiplicity, 2S+1, where S is the total spin angular momentum (sum of all the electron spins). Individual spins are denoted as spin up (s = +1/2) or spin down (s = -1/2).
- If we were to calculated the S for the excited singlet state, the equation would be 2(+1/2 + -1/2)+1 = 2(0)+1 = 1, therefore making the center orbital in the figure a singlet state.
- If the spin multiplicity for the excited triplet state was calculated, we obtain 2(+1/2 + +1/2)+1 = 2(1)+1 =3, which gives a triplet state as expected. he difference between a molecule in the ground and excited state is that the electrons is diamagnetic in the ground state and paramagnetic in the triplet state.

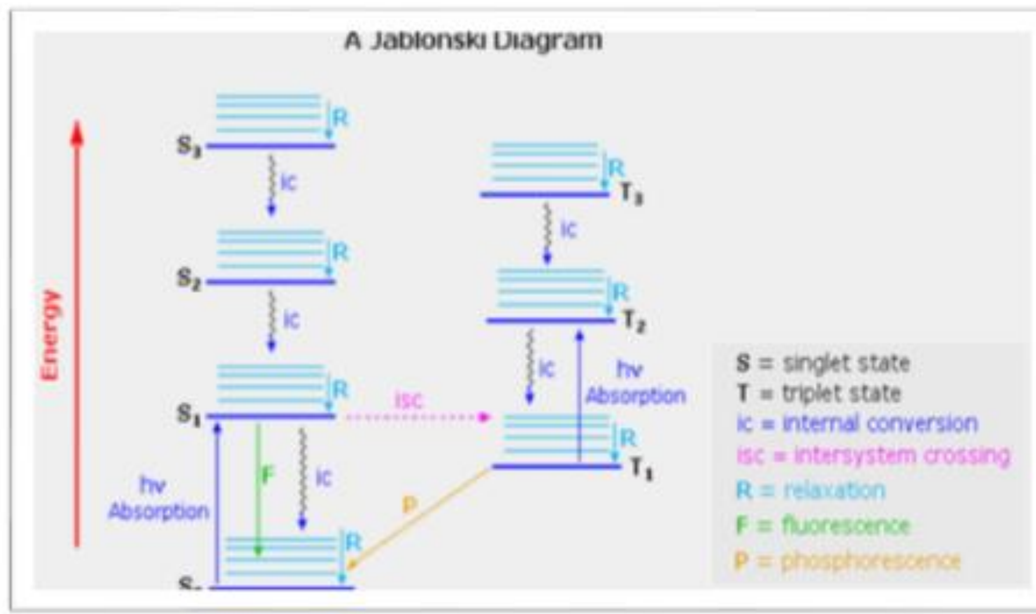
# Singlet and Triplet Excited State

- This difference in spin state makes the transition from singlet to triplet (or triplet to singlet) more improbable than the singlet-to-singlet transitions. This singlet to triplet (or reverse) transition involves a change in electronic state.
- For this reason, the lifetime of the triplet state is longer the singlet state by approximately 104 seconds fold difference.The radiation that induced the transition from ground to excited triplet state has a low probability of occurring, thus their absorption bands are less intense than singlet-singlet state absorption.
- The excited triplet state can be populated from the excited singlet state of certain molecules which results in phosphorescence. These spin multiplicities in ground and excited states can be used to explain transition in photoluminescence molecules by the Jablonski diagram.

# Jablonski Diagrams

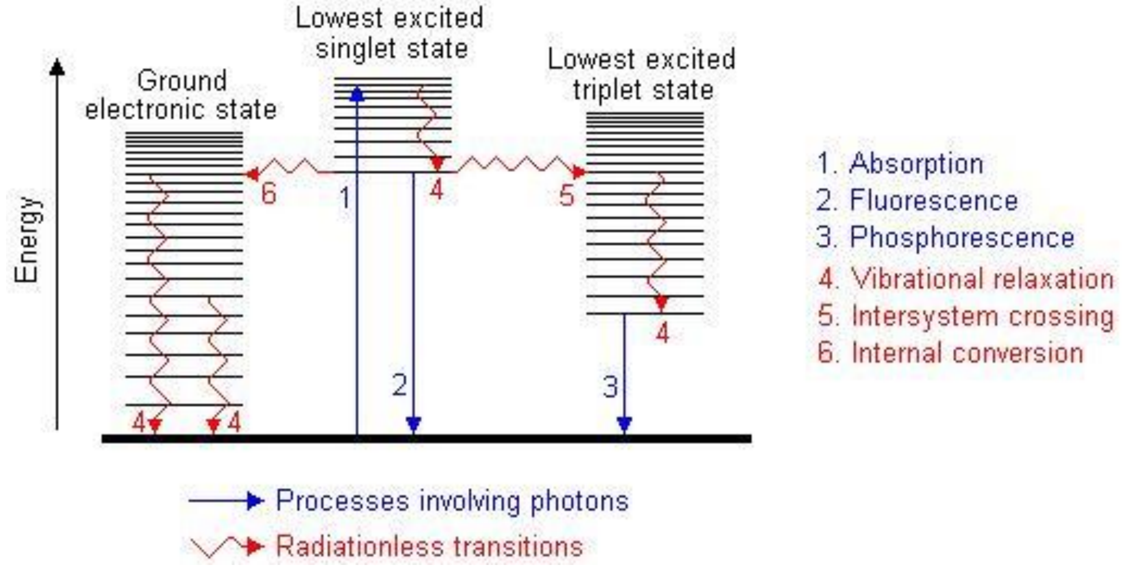
The Jablonski diagram that drawn below is a partial energy diagram that represents the energy of photoluminescent molecule in its different energy states.

The lowest and darkest horizontal line represents the ground-state electronic energy of the molecule which is the singlet state labeled as So . At room temperature, majority of the molecules in a solution are in this state.



- The upper lines represent the energy state of the three excited electronic states: S1and S2 represent the electronic singlet state (left) and T1 represents the first electronic triplet state (right). The upper darkest line represents the ground vibrational state of the three excited electronic state.
- The energy of the triplet state is lower than the energy of the corresponding singlet state.
- There are numerous vibrational levels that can be associated with each electronic state as denoted by the thinner lines. Absorption transitions can occur from the ground singlet electronic state (So) to various vibrational levels in the singlet excited vibrational states.
- It is unlikely that a transition from the ground singlet electronic state to the triplet electronic state because the electron spin is parallel to the spin in its ground state .

- This transition leads to a change in multiplicity and thus has a low probability of occurring which is a forbidden transition. Molecules also go through vibration relaxation to lose any excess vibrational energy that remains when excited to the electronic states ( S1 and S2 ) as demonstrated in wavy lines
- The knowledge of forbidden transition is used to explain and compare the peaks of absorption and emission.

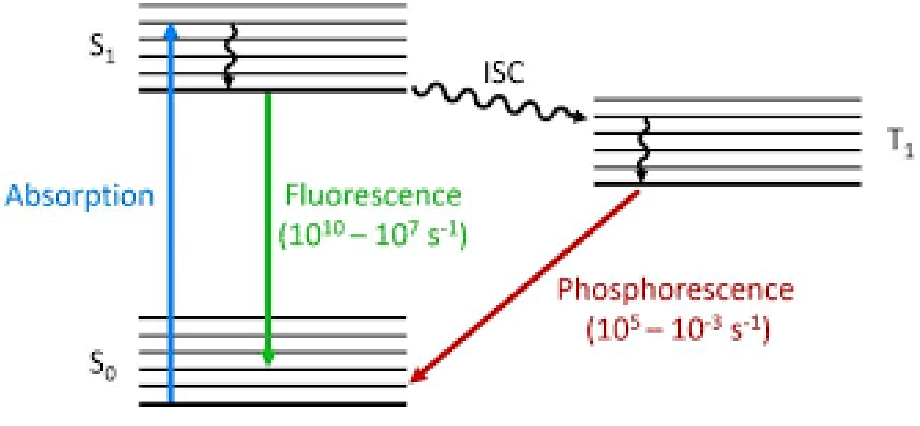


# Absorption and Emission Rates

❖ The rate of photon absorption is very rapid.
Fluorescence emission occurs at a slower rate.

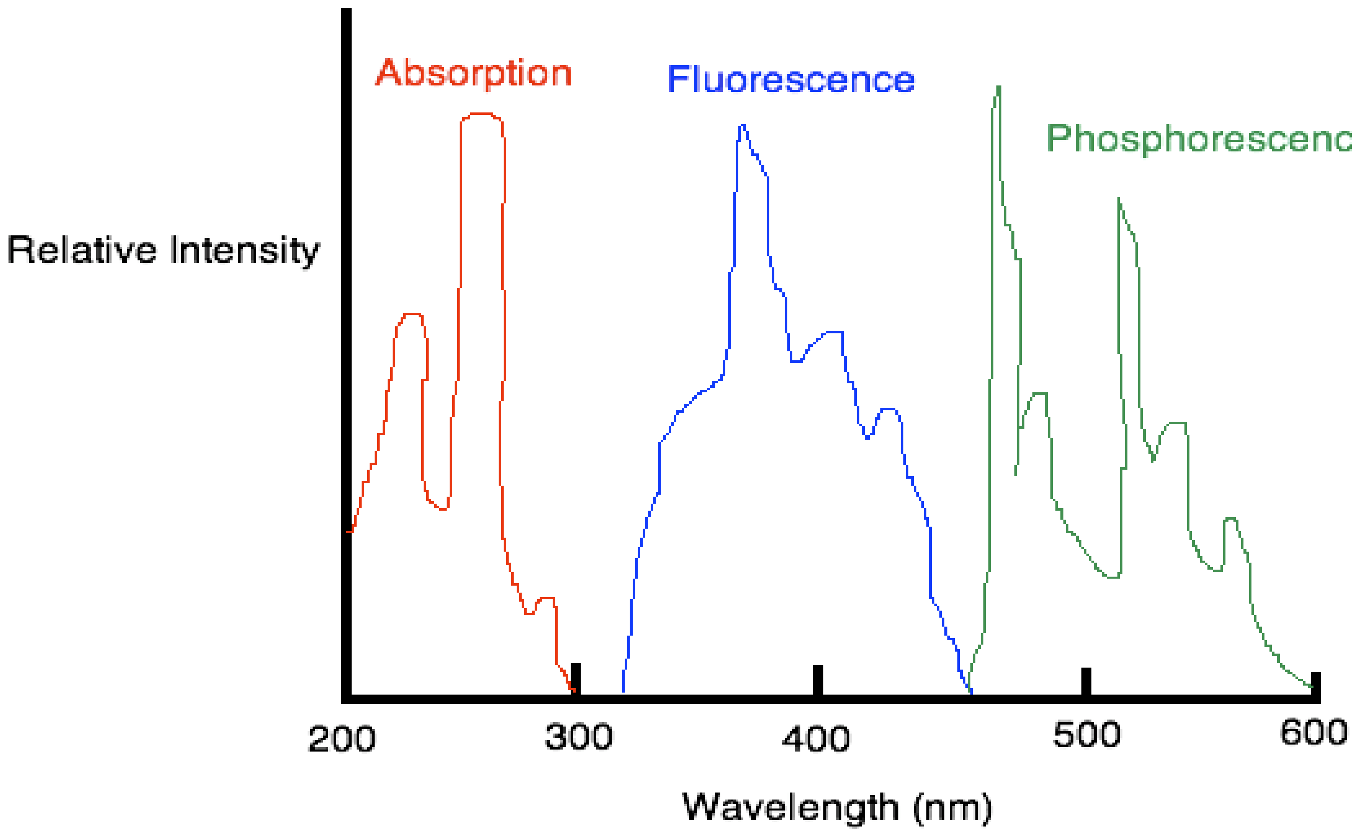
Since the triplet to singlet (or reverse) is a forbidden transition, meaning it is less likely to occur than the singlet-to-singlet transition, the rate of triplet to singlet is typically slower.

❖ Therefore, phosphorescence emission requires more time than fluorescence.



# Emission and Excitation Spectra

- ❖ One of the ways to visually distinguish the difference between each photoluminescence is to compare the relative intensities of emission/excitation at each wavelength.
- ❖ An example of the three types of photoluminescence (absorption, fluorescence and phosphorescence) is shown for phenanthrene in the spectrum below.
- ❖ In the spectrum, the luminescent intensity is measure in a wavelength is fixed while the excitation wavelength is varied. The spectrum in red represents the excitation spectrum, which is identical to the absorption spectrum because in order for fluorescence emission to occur, radiation needs to be absorbed to create an excited state.
- ❖ The spectrum in blue represent fluorescence and green spectrum represents the phosphorescence.




Wavelength Intensities of Absorption, Fluorescence, and Phosphorescence

- Fluorescence and Phosphorescence occur at wavelengths that are longer than their absorption wavelengths.
- Phosphorescence bands are found at a longer wavelength than fluorescence band because the excited triplet state is lower in energy than the singlet state.
- The difference in wavelength could also be used to measure the energy difference between the singlet and triplet state of the molecule. The wavelength ( $\lambda$ ) of a molecule is inversely related to the energy ( E ) by the equation below:

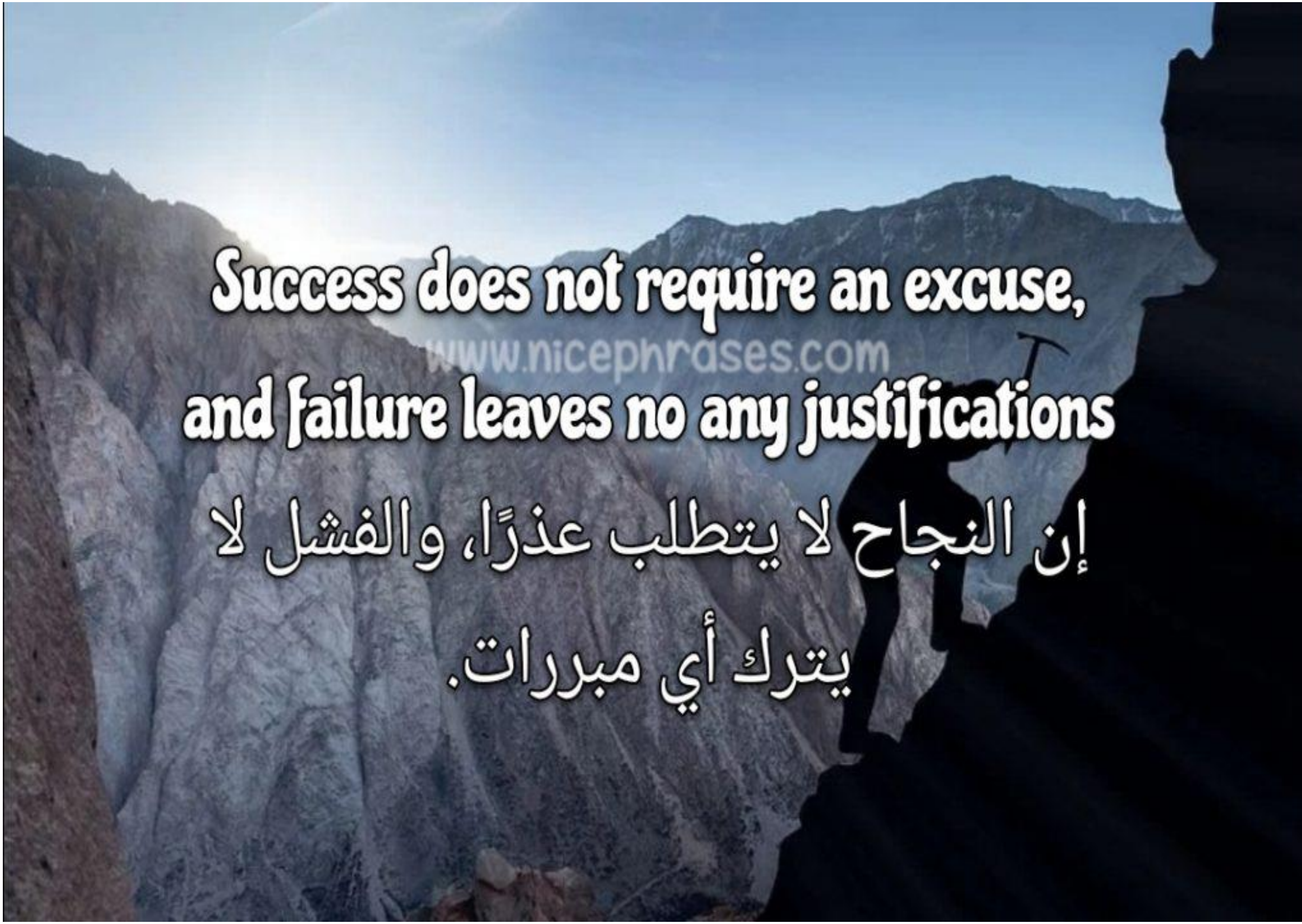
$$\mathbf{E=hc\lambda(8)}$$

- As the wavelength increases, the energy of the molecule decrease and vice versa.

# Fluorescence vs Phosphorescence

More Information Online WWW.DIFFERENCEBETWEEN.COM

| | Fluorescence | Phosphorescence |
|---|---|---|
| DEFINITION | The emission of light by a substance that has absorbed light or other electromagnetic radiation. | The light emitted by a substance without combustion or perceptible heat. |
| TIME | Stops as soon as we take away the light source. | Tends to stay little longer even after we remove the irradiating light source. |
| MECHANISM | Takes place when excited energy is released, and the molecule comes back to the ground state from the singlet-excited stage. | Takes place when a molecule is coming back to the ground state form the triplet excited state (metastable state). |
| ENERGY RELEASED | Is higher than that in the phosphorescence. | Is lower than that in the fluorescence. |
| RELATIONSHIP BETWEEN THE ABSORBED AND RELEASED ENERGY | The absorbed amount of energy is released back. | Released energy is lower than what is absorbed. |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