

## 2-Electronic Spectroscopy



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Marea Roja en California, algas fluorescentes

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# 1-ELECTRONIC SPECTROSCOPIES

ELECTRONIC LEVELS OF THE MATTER → EMR uv-vis

$\lambda$ : 10-1000 nm  
uv: 10-350 nm  
Vis: 350-1000 nm

**ATOMIC:** *Absorption*

*Emission:* **Emission Spectroscopy**  
**Flame Spectroscopy**

**MOLECULAR:** *Absorption*

*Emission:* **Fluorescence**  
**Phosphorescence**

## 2. BONDS AND ELECTRONIC MOLECULAR LEVELS

**BOND:** SHARING OF ONE ELECTRON PAIR

**MOLECULAR ORBITAL :** ADDITION OF ATOMIC ORBITALS

**BONDING**

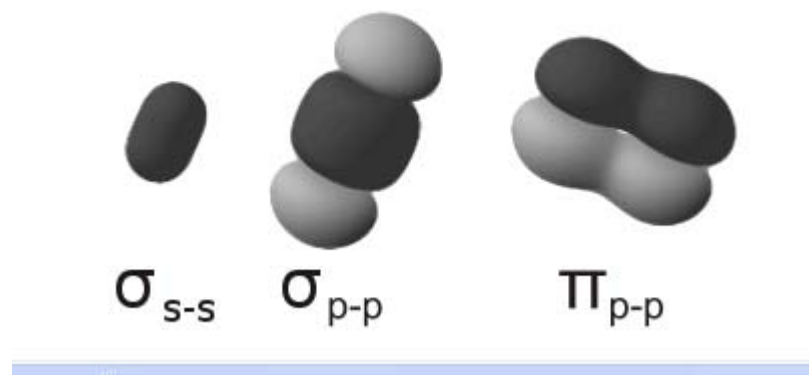
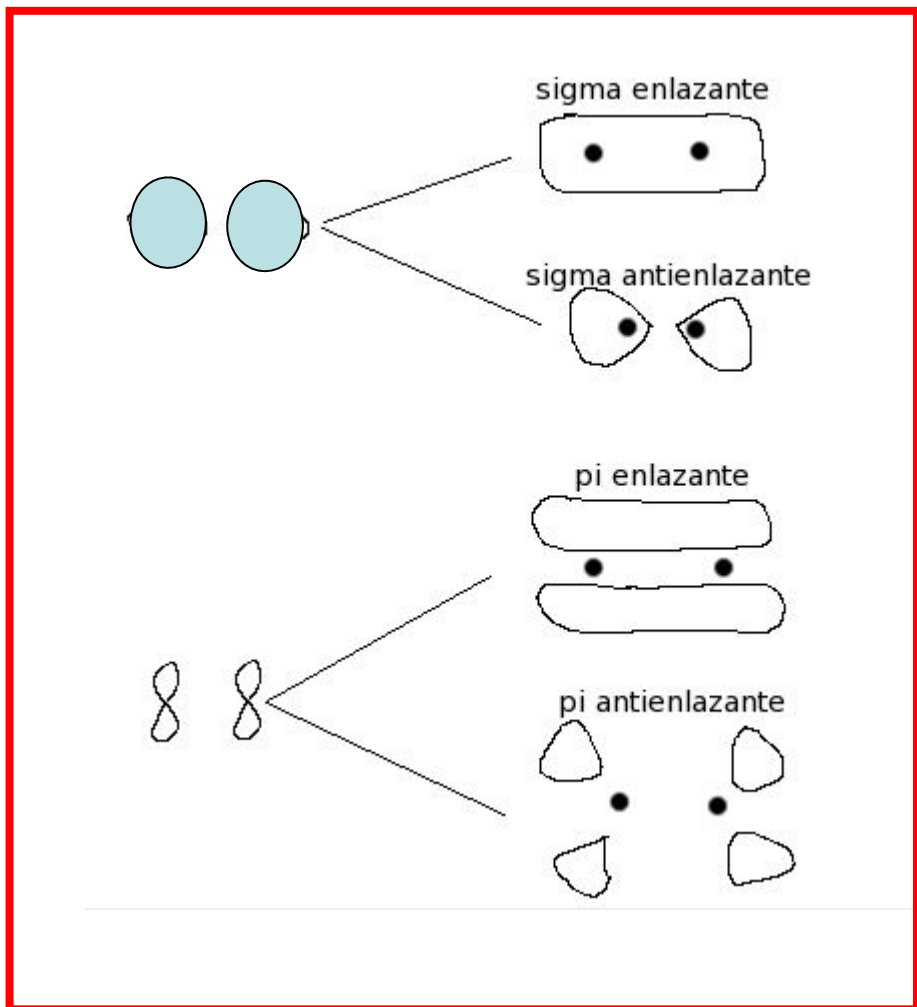


**ANTI-BONDING**

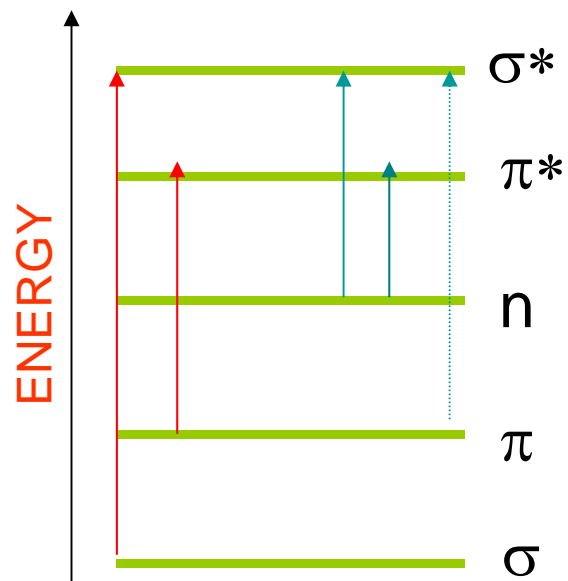


$\sigma$ : single bond  
 $\pi$ : multiple bond

## 2. BONDS AND ELECTRONIC MOLECULAR LEVELS



# 3- MOLECULAR ELECTRONIC TRANSITIONS



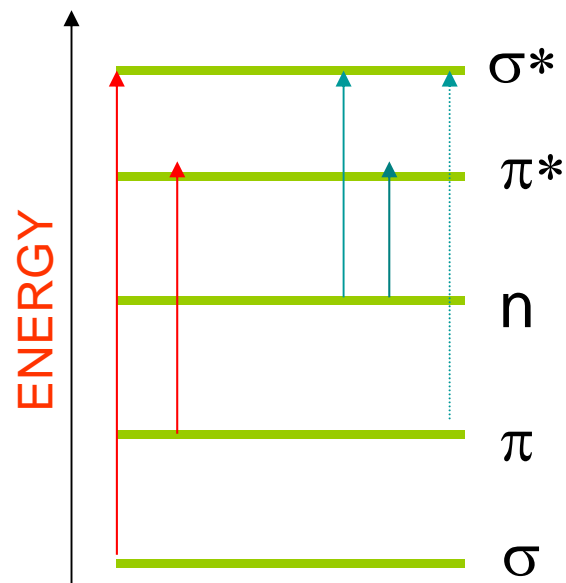
## SELECTIVITY RULES

- CONSTANT GEOMETRY
- CONSTANT MULTIPLICITY

## TRANSITION PROBABILITY

$$\pi \rightarrow \sigma^* < n \rightarrow \sigma^*; n \rightarrow \pi^*$$

# 3. MOLECULAR ELECTRONIC TRANSITIONS



uv-vis: 10 nm-1000nm

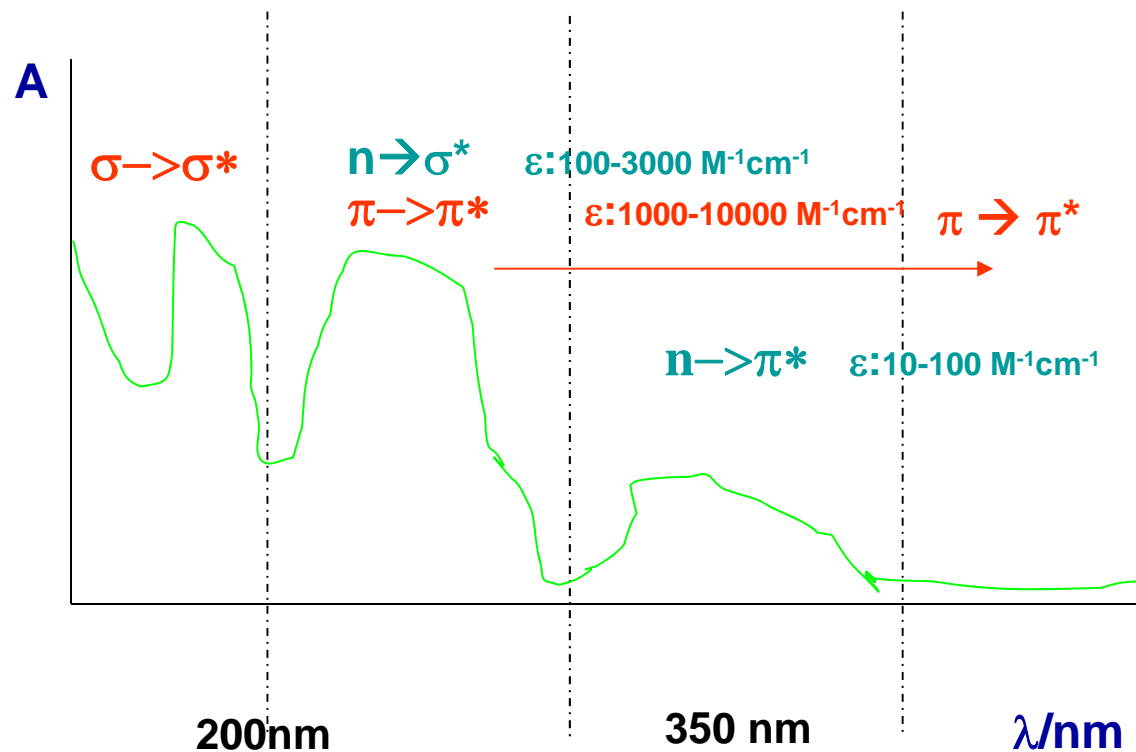
FAR (VACUUM): 10-200 nm

NEXT: 200-350 nm

uv A: 330- 400 nm

uv B: 280-330 nm

uv C: 200-280 nm

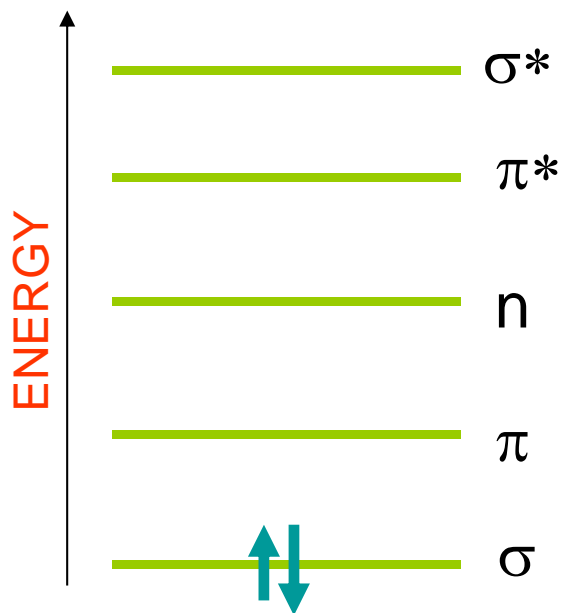


## SELECTION RULES

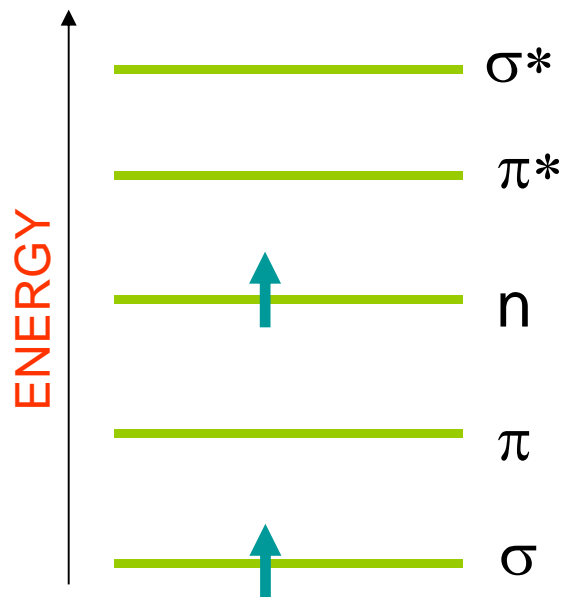
- **CONSTANT GEOMETRÍA**
- **CONSTANT MULTIPLICITY**

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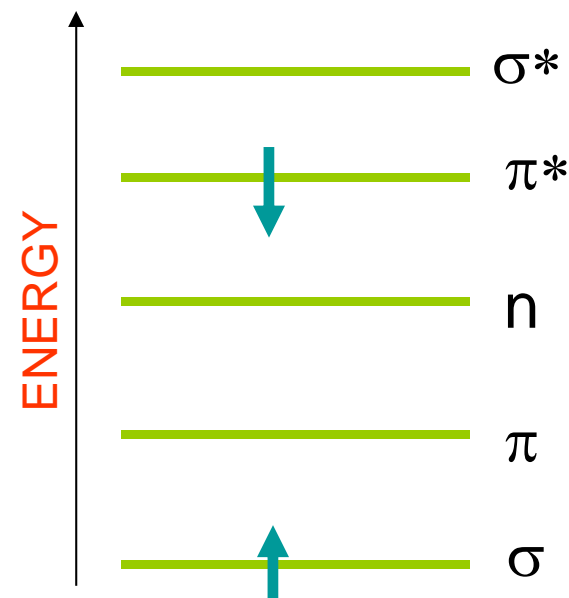
# 4. MULTIPLICITY



**EEF:**  
 $S = 1/2 - 1/2 = 0$   
 $(2S+1) = 1$   
**SINGLET**



**EEE:**  
 $S = 1/2 + 1/2 = 1$   
 $(2S+1) = 3$   
**TRIPLET**



**EEE:**  
 $S = 1/2 - 1/2 = 0$   
 $(2S+1) = 1$   
**SINGLET**



# 5. MOLECULAR uv-vis EMISSION SPECTROSCOPY

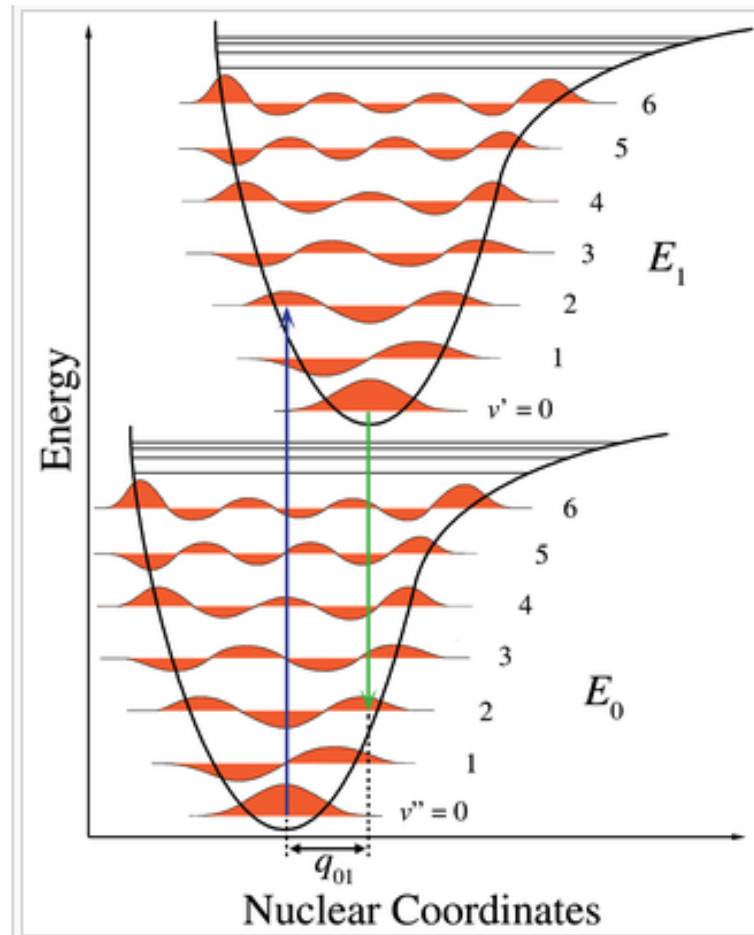
## LUMINESCENCE

- *Bioluminescence*: Chemical Reaction.
- *Thermoluminescence*: Temperature
- *Photoluminescence*: Light

# 6. PROCESSES INVOLVED IN MOLECULAR uv-vis EMISSION SPECTROSCOPY

1º ABSORCIÓN:  $10^{-14}$ - $10^{-15}$  s

## PRINCIPIO DE FRANK CONDON



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# 6. PROCESSES INVOLVED IN MOLECULAR uv-vis EMISSION SPECTROSCOPY

## 2<sup>o</sup> DEACTIVATION OF THE EXCITED STATE:

### 2.A. PHOTOPHYSICS PROCESSES

#### *Non Radiative:*

Heat

IC: internal conversion

ISC: inter-system crossing

#### - *Radiative:*

Fluorescence

Phosphorescence

#### - *Energy Transfer:*

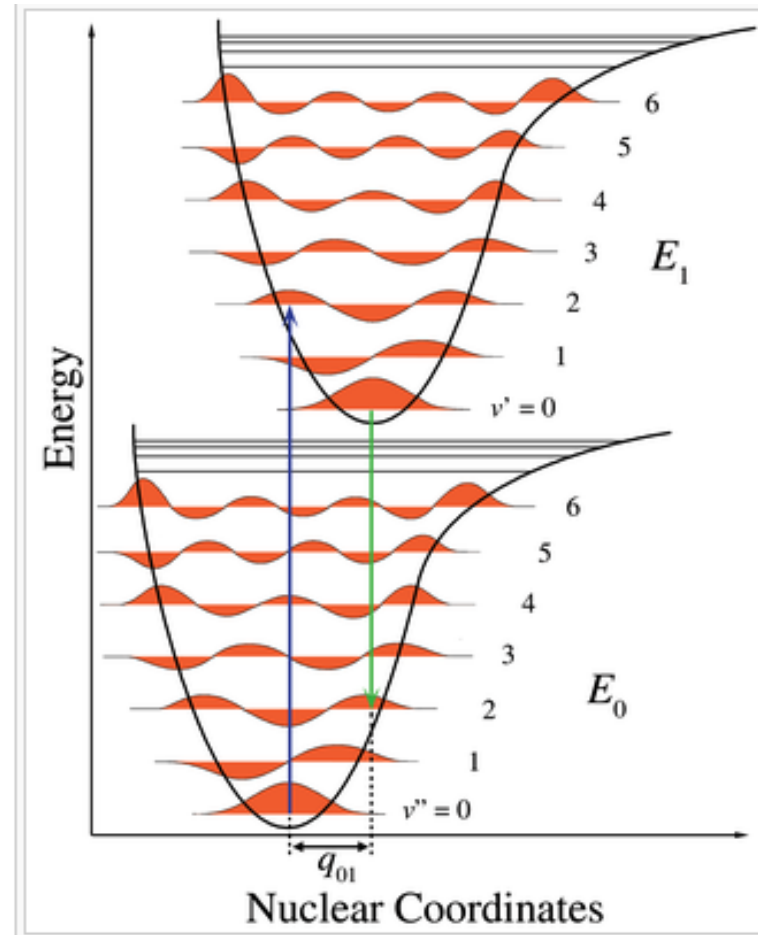
quenching, FRET

### 2.B. PHOTOCHEMICAL PROCESSES

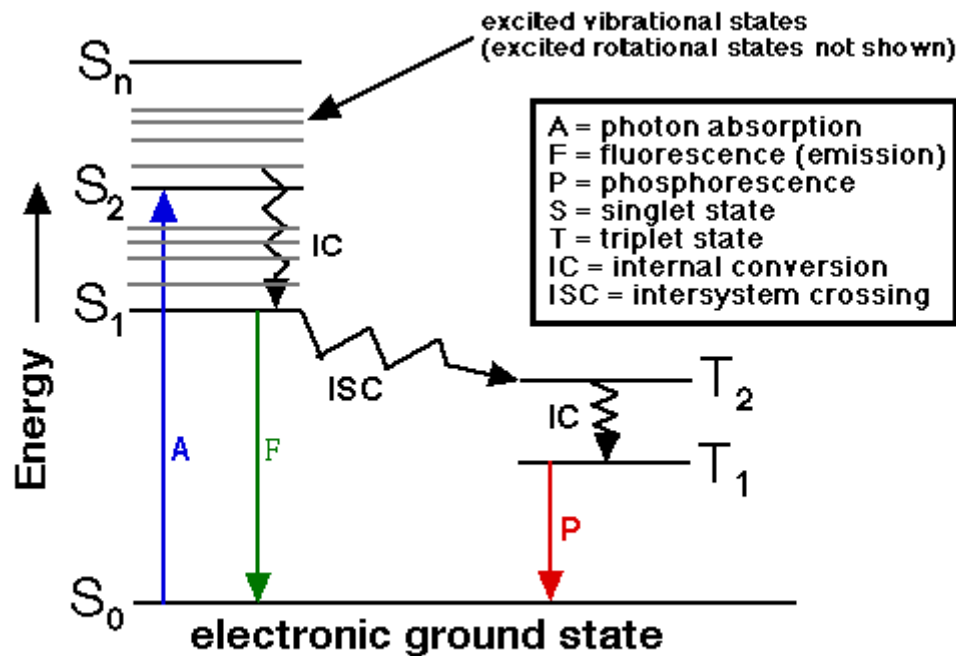
- Pre-dissociation
- Dissociation
- Chemical Reactions

# 7. PHOTOCHEMICAL PROCESSES

- Pre-dissociation
- Dissociation
- Chemical Reactions



# 8. RADIATIVE AND NON-RADIATIVE DEACTIVATION ROUTES



**IC:**  $10^{-12}$   
 $\tau_S = 10^{-9} - 10^{-6}$  s  
 $\tau_T = 10^{-4}$  s

## Jablonsky Plott

### Non Radiative:

Heat

IC: internal conversion

ISC: inter-system crossing

### - Radiative:

Fluorescence

Phosphorescence

## 9. DEACTIVATION BY ENERGY TRANSFER

### 8.A. QUENCHING



### 8.B. FRET: Fluorescence Resonance Energy Transfer



#### LIMITING CONDITION:

- The absorption spectrum of the acceptor should overlap to the emission spectrum of the donor.

## 12. BIBLIOGRAPHY

1. **Principios de Análisis Instrumental**, [Douglas A. Skoog](#), [Stanley R. Crouch](#), [F. James Holler](#) , Méjico, 2008.

Bibliografía general

2. **Principles of Fluorescence Spectroscopy**. Joseph Lakowicz. Plenum Press, New York (3<sup>rd</sup>. edición)