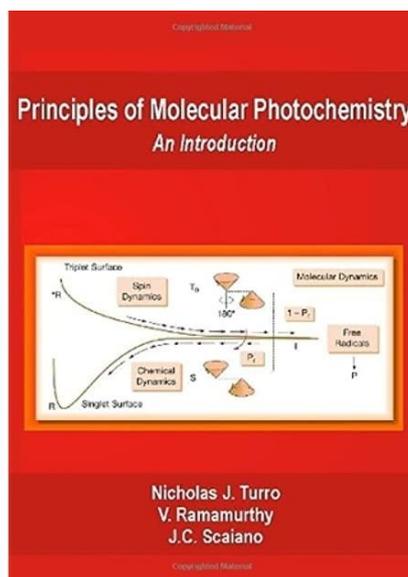
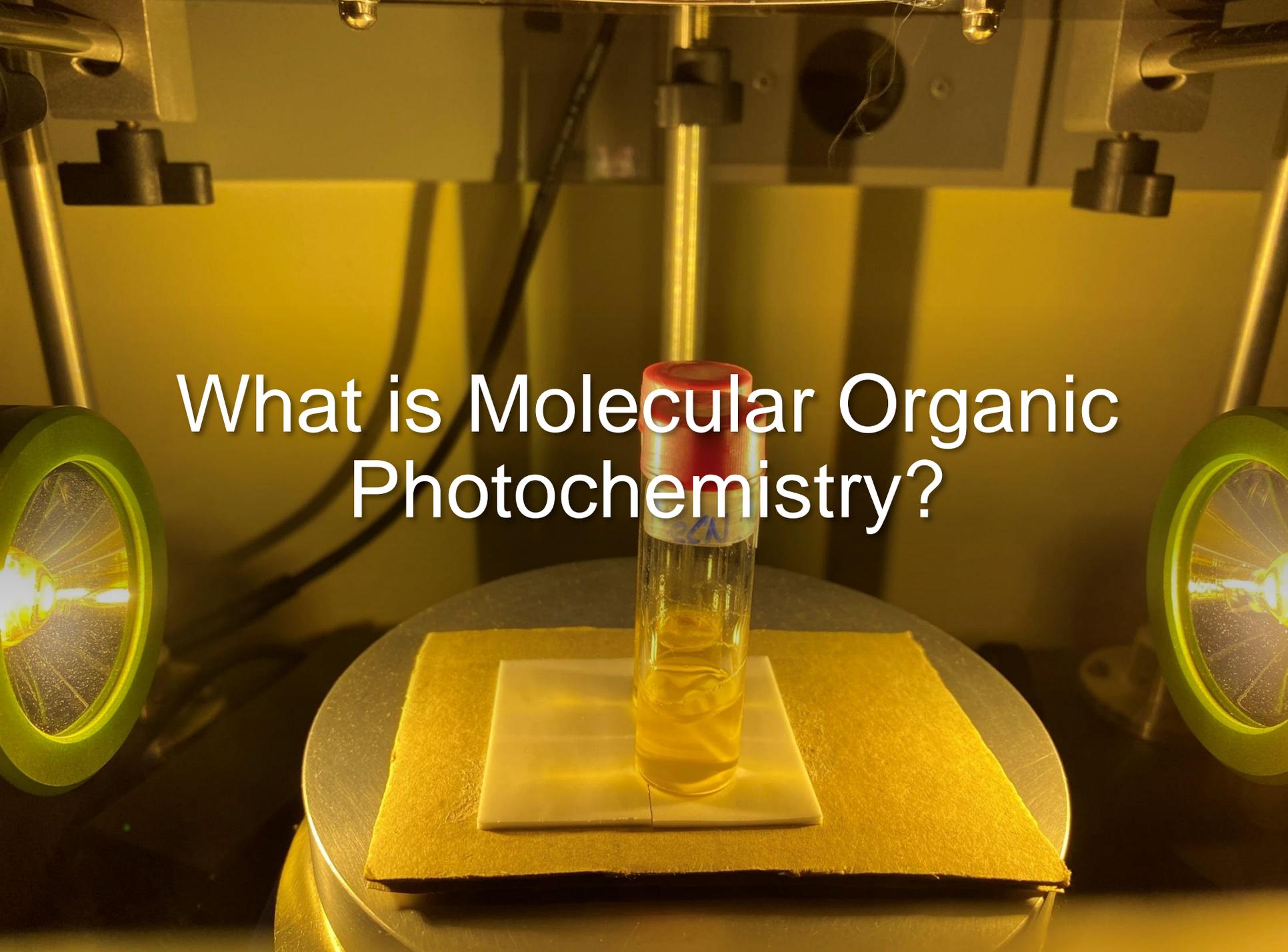


Chapter 1: Molecular Photochemistry of Organic Compounds

An Overview



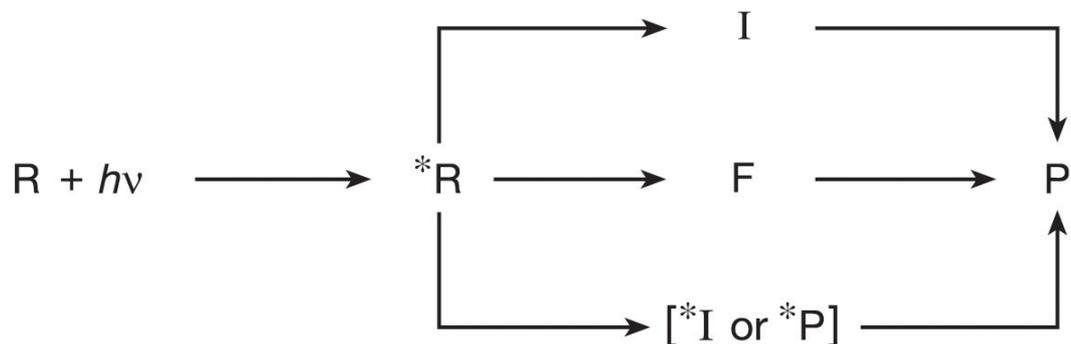


What is Molecular Organic
Photochemistry?

What is Molecular Organic Photochemistry?

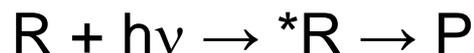
- Molecular organic photochemistry is a science concerned with the structures and dynamic processes that result from the interaction of light with organic molecules
- The field of molecular organic photochemistry can be classified in terms of the *photophysics of organic compounds* (the interactions of light and organic molecules resulting in net physical changes) and the *photochemistry of organic compounds* (the interactions of light and organic molecules resulting in net chemical changes)
- Rather broad and interdisciplinary topic embracing many fields
 - Chemical physics, spectroscopy, physical organic chemistry, synthetic organic chemistry, computational chemistry, and supramolecular chemistry

What is Molecular Organic Photochemistry?



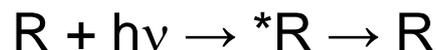
Scheme 1.2 copyright 2009 University Science Books

Molecular organic photochemistry involves the overall process



where R is an organic molecule that absorbs a photon ($h\nu$), whose frequency (ν) is correct for light absorption by R ; $*R$ is an electronically excited molecule, and P is an isolated product(s)

Organic photophysics involves



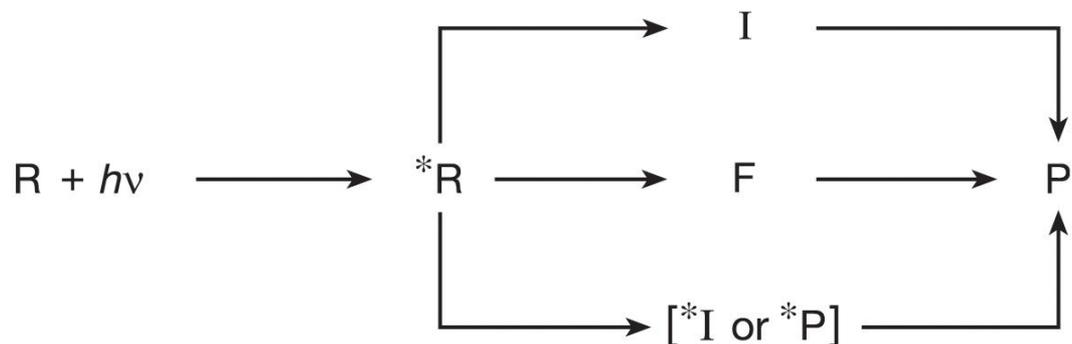
where R absorbs the photon but does not undergo chemical change

What is Molecular Organic Photochemistry?

- **Important:** While not stated explicitly, it should be assumed that the reactions described in this course are conducted in a solution of an inert solvent at or near room temperature ($\sim 25\text{ }^{\circ}\text{C}$), unless stated otherwise



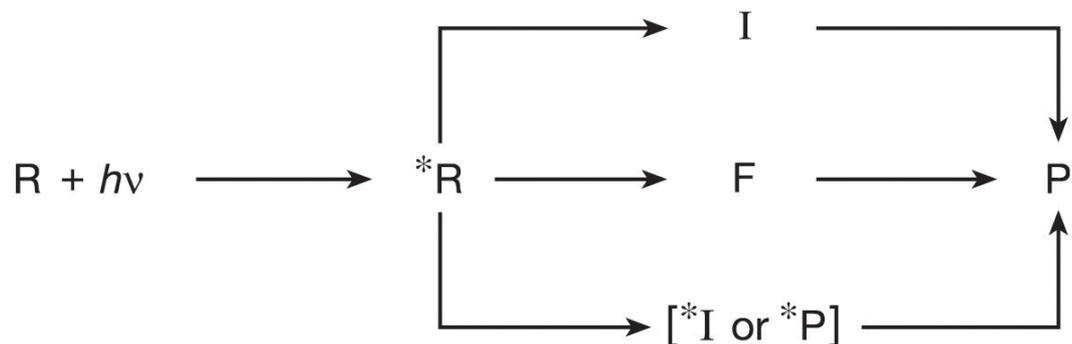
A Global Paradigm



Scheme 1.2 copyright 2009 University Science Books

- This scheme provides a paradigm that serves as a basis for *analyzing all organic photochemical reactions and photophysical processes*
- We will employ the term *molecular photochemistry* to include **both** the photophysics of $*R$ and the photochemistry of $*R$
 - To have a proper understanding of the photochemistry of $*R$, we must also develop an understanding of the photophysics of $*R$

A Global Paradigm



Scheme 1.2 copyright 2009 University Science Books

- Our scheme shows that there are *three* fundamentally distinct pathways, termed *primary photochemical processes*, that $*R$ can follow on the way to P

A Global Paradigm



Scheme 1.2 copyright 2009 University Science Books

1. $*R \rightarrow I \rightarrow P$

- Forms a discrete reactive intermediate (I) that can typically be described as having the characteristics of a radical pair (RP), a biradical (BR), or a zwitterion (Z)

Of the three possibilities, this pathway is the most commonly observed pathway for photochemical reactions

A Global Paradigm

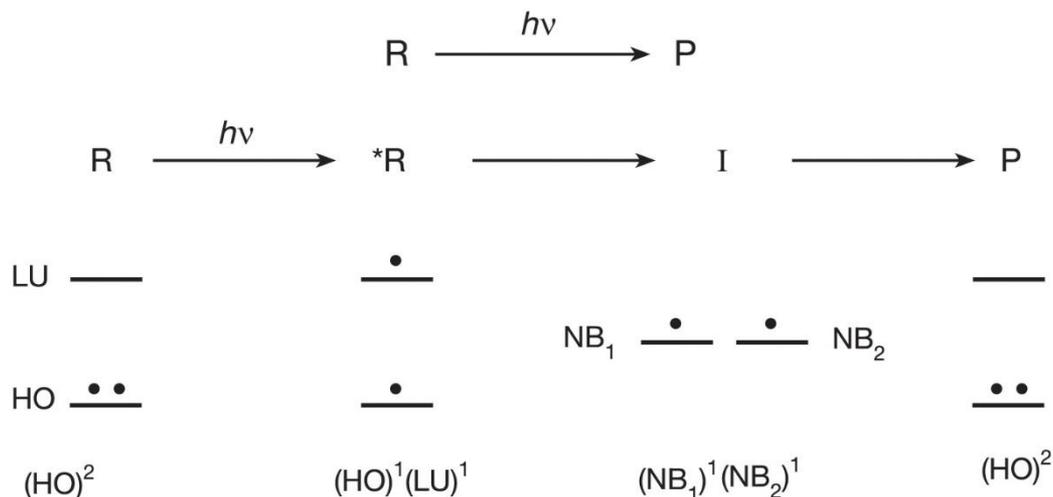


Scheme 1.2 copyright 2009 University Science Books

2. ${}^*R \rightarrow F \rightarrow P$

- Does not involve a discrete reactive intermediate (I), but instead proceeds through a “funnel” (F)
- This pathway can be described in the language of energy surfaces as a “conical surface intersection” or as a minimum produced by surface-avoided intersections

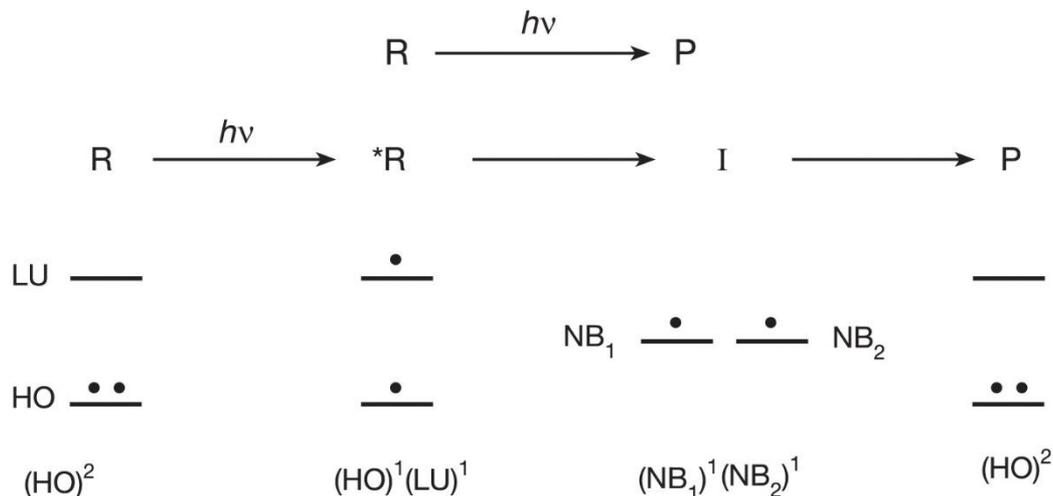
From a Global Paradigm to the Everyday Working Paradigm



Scheme 1.2 copyright 2009 University Science Books

- Let's now examine the most common pathway, $R + h\nu \rightarrow *R \rightarrow I \rightarrow P$, in more detail
- We have now elaborated on our original scheme to energy levels of the **HOMO** (highest occupied molecular orbital) and **LUMO** (lowest unoccupied molecular orbital) of R, *R, I and P
- The scheme *qualitatively* shows the energies of the HOMO and LUMO, and electron spin is not considered at this stage

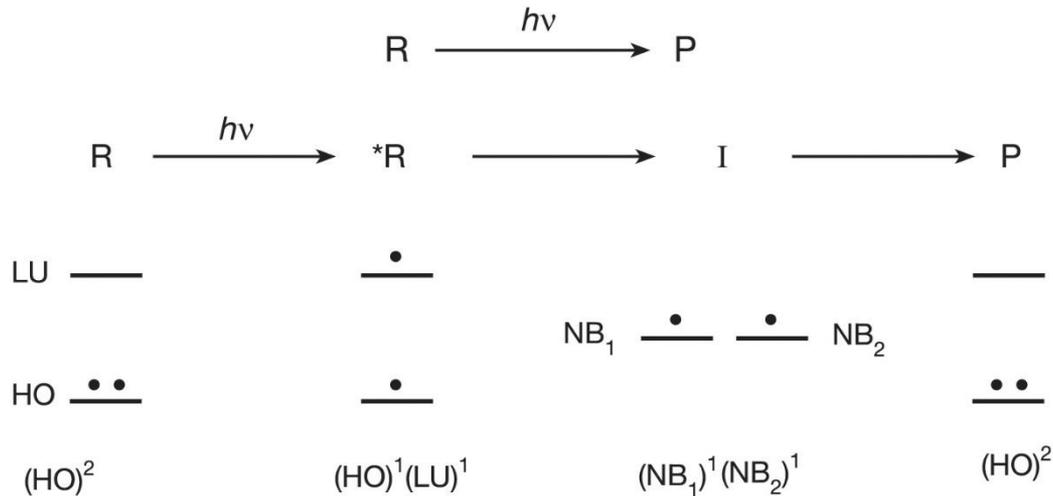
From a Global Paradigm to the Everyday Working Paradigm



Scheme 1.2 copyright 2009 University Science Books

- The energies of the HOMO and LUMO for R, *R , and P are assumed to be far apart (typically > 40 kcal/mol), whereas the *energies between the HOMO and LUMO molecular orbitals of I are assumed to be very similar, and may often be approximated as non-bonding (NB) orbitals*
- It is assumed that all remaining electrons that are not shown in this scheme are spin-paired (according to the **Pauli exclusion principle**) in orbitals of lower energy
- Lower energy electrons are often difficult to perturb, even in photochemical processes, so they are of secondary importance in determining photochemical and photophysical processes

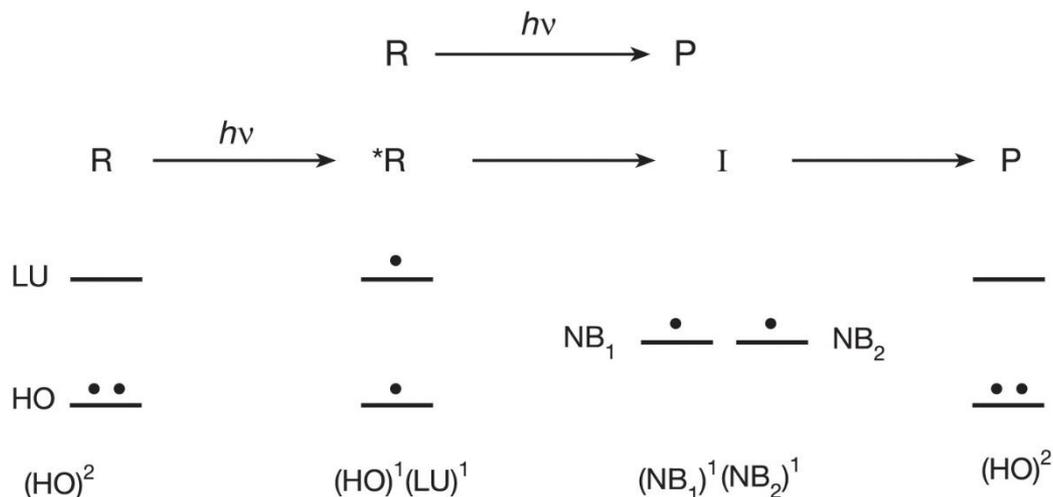
From a Global Paradigm to the Everyday Working Paradigm



Scheme 1.2 copyright 2009 University Science Books

- The starting point for a photochemical/photophysical process is the assignment of the electronic nature of HO and LU of R and *R
- This amounts to assigning a specific electron configuration of $R(\text{HO})^2$ and $*R(\text{HO})^1(\text{LU})^1$
- I is generally a species possessing two NB orbitals that are produced by the primary photochemical process $*R \rightarrow I(\text{NB}_1)^1(\text{NB}_2)^1$
- There are no HO and LU of different energies in the latter case, but instead two NB orbitals of equal energy

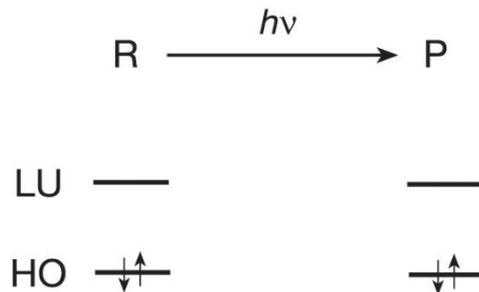
From a Global Paradigm to the Everyday Working Paradigm



Scheme 1.2 copyright 2009 University Science Books

- When the two NB orbitals are located primarily on carbon atoms, the lowest energy orbital configuration of I corresponds to one electron in each NB orbital, thus producing a **radical pair (RP)** or **biradical (BR)**
- Note: the terms ‘biradical’ and ‘diradical’ are often used interchangeably, and refer to a situation where both NB orbitals are located on the same molecular structure
- We will use the symbol “D” to mean a more general “diradicaloid” (either a RP or BR) in the upcoming schemes

Singlet States, Triplet States, Diradicals and Zwitterions

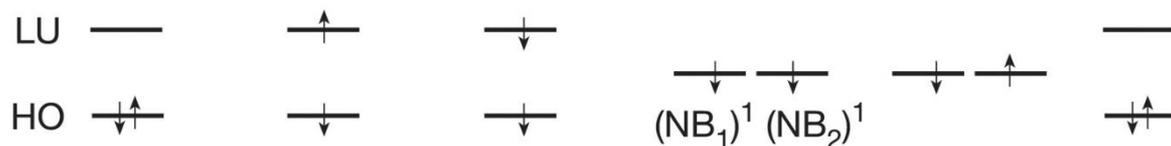
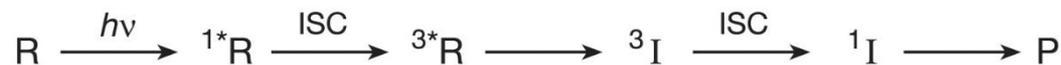


- This electronic configurations of the ground states of R and P are generally $(HO)^2(LU)^0$ for ordinary organic molecules

Question: Can you think of a molecule that is an exception?

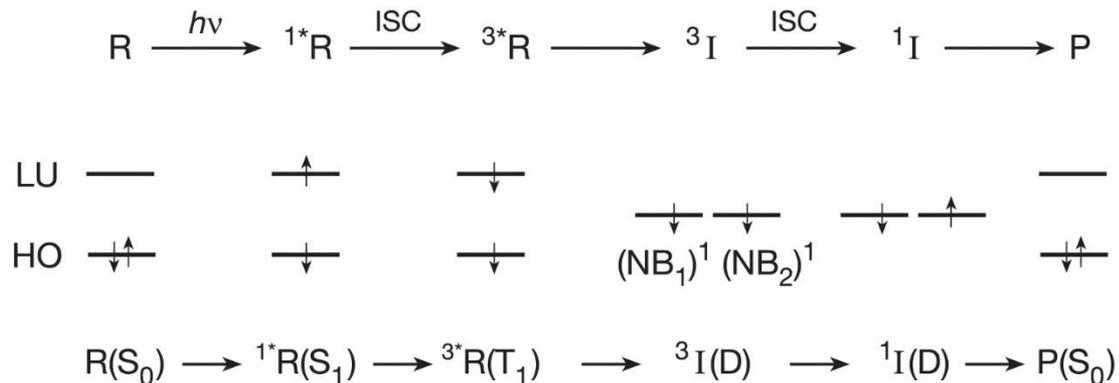
- According to the **Pauli exclusion principle**, the spins of the two electrons in the same orbital must be paired
 - Symbolized as $\uparrow\downarrow$
 - Termed “antiparallel spins”
 - Corresponds to a singlet spin configuration or singlet state

Singlet States, Triplet States, Diradicals and Zwitterions



- The electronic configuration of *R and I , both of which typically possess one electron in each of the two key orbitals, are not required by the Pauli exclusion principle to be spin paired
- The two key electrons in the half-filled orbitals can be either paired ($\uparrow\downarrow$, singlet state) or unpaired (symbolized as $\uparrow\uparrow$, termed “parallel spins”, corresponding to a triplet spin configuration or triplet state)

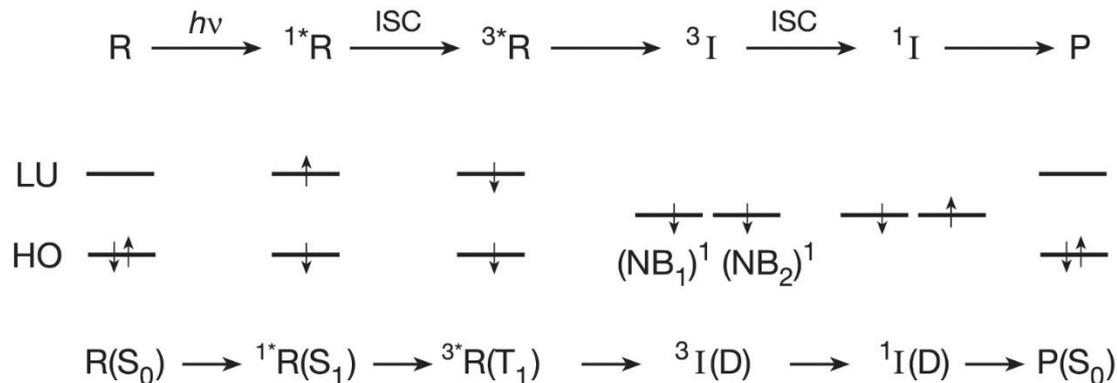
Singlet States, Triplet States, Diradicals and Zwitterions



Scheme 1.3 copyright 2009 University Science Books

- The *singlet states* of a molecule are given the symbol S_n , where the subscript n ranks the energy of the singlet state
- The subscript 0 is reserved for the lowest-energy electronic ground state, which is always a singlet state (i.e. S_0) for ordinary organic molecules
- The first excited singlet state is S_1 , the second excited singlet state is S_2 , etc.

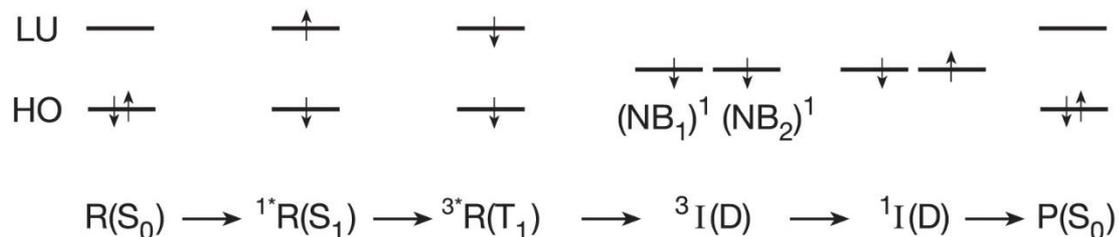
Singlet States, Triplet States, Diradicals and Zwitterions



Scheme 1.3 copyright 2009 University Science Books

- When *R (or I) possesses two orbitally unpaired electrons and the electron spins are unpaired ($\uparrow\uparrow$), the structure is termed a *triplet state* and labeled T_n , where the subscript n ranks the energy of the triplet state
- Since the subscript 0 is reserved for the lowest-energy electronic ground state (S_0), n = 1, 2, etc. for triplet states
- The terms 'singlet' and 'triplet' originate from the magnetic properties of electron spins (Chapter 2)

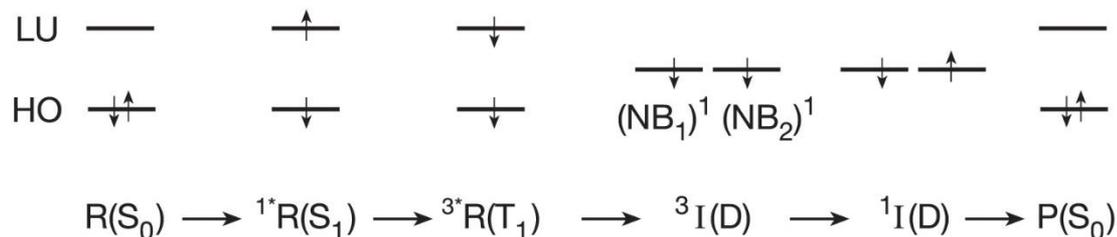
Singlet States, Triplet States, Diradicals and Zwitterions



Scheme 1.3 copyright 2009 University Science Books

- In general, R and P represent the singlet ground states of organic molecules, so they are given the symbol $R(S_0)$ and $P(S_0)$
- If the electrons are spin paired ($\uparrow\downarrow$) in *R , this is the *singlet excited state* and labeled S_1 , where the subscript indicates that the state is the first singlet excited state [${}^1{}^*R(S_1)$ above]
- If the electron spins are parallel ($\uparrow\uparrow$) in *R , this is a *triplet excited state* and is labeled T_1 , where the subscript indicates that the state is the first triplet excited state [${}^3{}^*R(T_1)$ above]

Singlet States, Triplet States, Diradicals and Zwitterions



Scheme 1.3 copyright 2009 University Science Books

- Likewise, I with one electron in two NB orbitals may be either a singlet ${}^1I(\uparrow\downarrow)$ or triplet ${}^3I(\uparrow\uparrow)$
- Reminder: the symbol D (for diradical) is a general label for a reactive intermediate (I) that possesses two half-filled orbitals (typically NB) of comparable energy
 - D represents both RP, where one radical center is located on two molecular fragments, and BR, where two radical centers are located on the same molecular structure
- The I(D) species differ from *R , because *R possesses two half-filled orbitals of *very different energies*

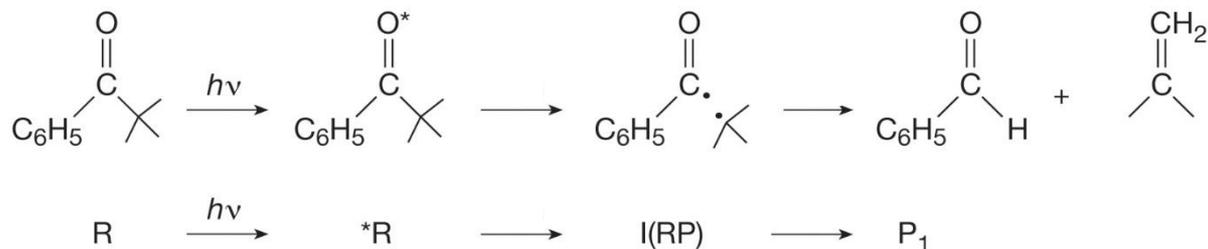
Singlet States, Triplet States, Diradicals and Zwitterions

- If I is in the singlet state, it is also possible for the two electrons to be in one NB orbital and none in the other
 - $I(\text{NB})^2(\text{NB})^0$
- Such a species is referred to as a **zwitterion** and given the symbol **I(Z)**
- The I(Z) species are involved in the $^1R \rightarrow ^1I(Z)$ and the $^1R \rightarrow F$ (where F = funnel) steps of photoreactions involving certain singlet states
- D species are always involved in the $^3R \rightarrow ^3I(D)$ step of photochemical reactions involving photochemical processes initiated by 3R
- The rules for D and Z formation and the chemical properties of these species will be discussed in Chapter 6

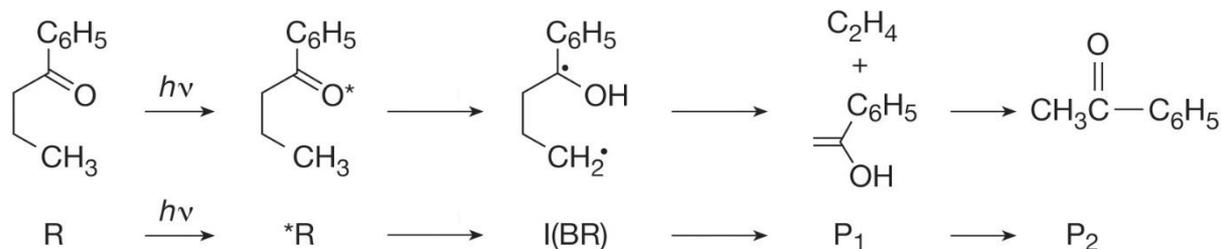
An Example: Norrish Reactivity

- The figure below represents two concrete examples of $*R \rightarrow I(D)$ primary photochemical processes
- In the first example (a), the **Norrish Type I reaction**, $*R$ undergoes an α -cleavage of the C–C bond of the C=O functional group to produce a radical pair, I(RP)
- In the second example (b), the **Norrish Type II reaction**, $*R$ undergoes an intramolecular H-abstraction to produce a biradical, I(BR)

(a) Norrish Type I reaction: I(D) = radical pair, I(RP)

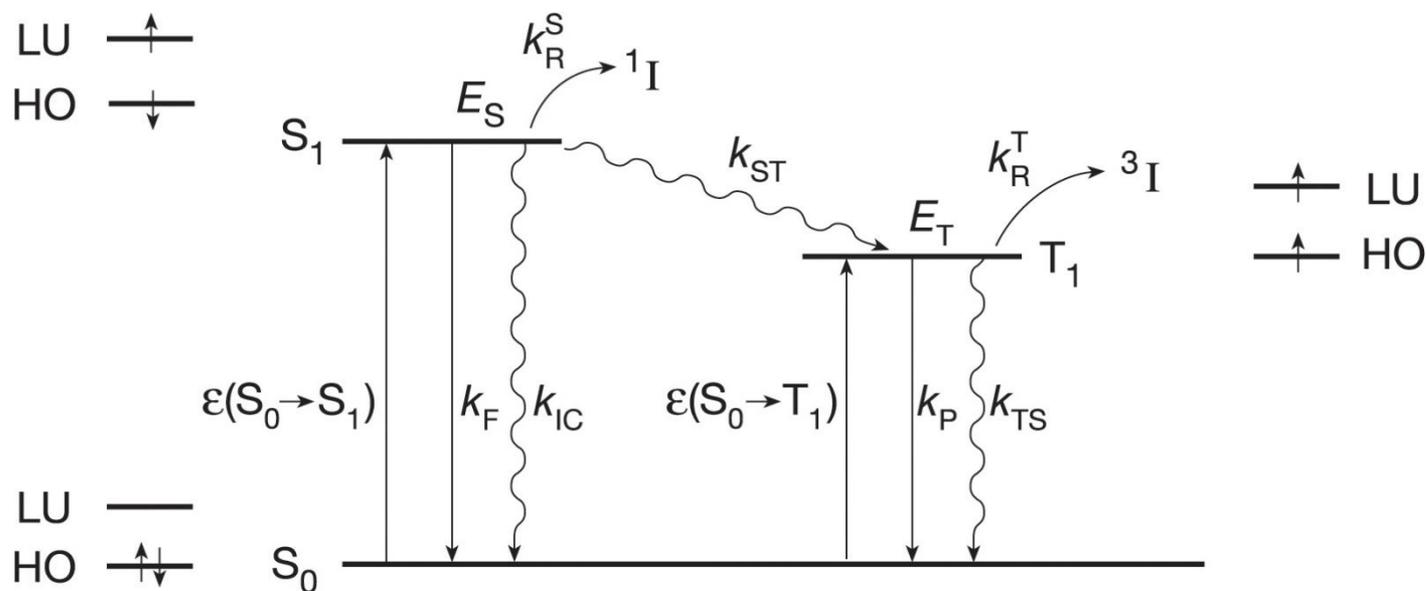


(b) Norrish Type II reaction: I(D) = biradical, I(BR)



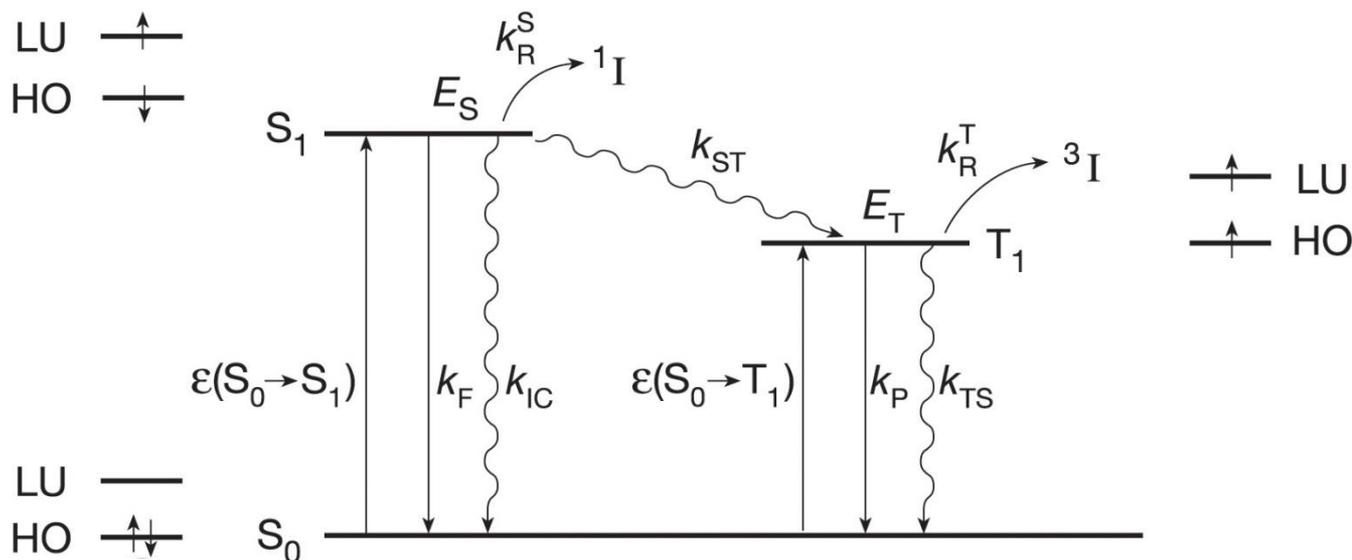
State Energy Diagrams

- According to the previous scheme (Scheme 1.3 of text), there are three important molecular states, $R(S_0)$, $^*R(S_1)$ and $^*R(T_1)$, that must always be considered when analyzing a photochemical reaction involving organic molecules
- A *state energy diagram* (see below) provides a compact way of displaying the relative energies and keeping track of the S_0 , S_1 and T_1 of an organic molecule
 - E_S is the energy of S_1 and E_T is the energy of T_1



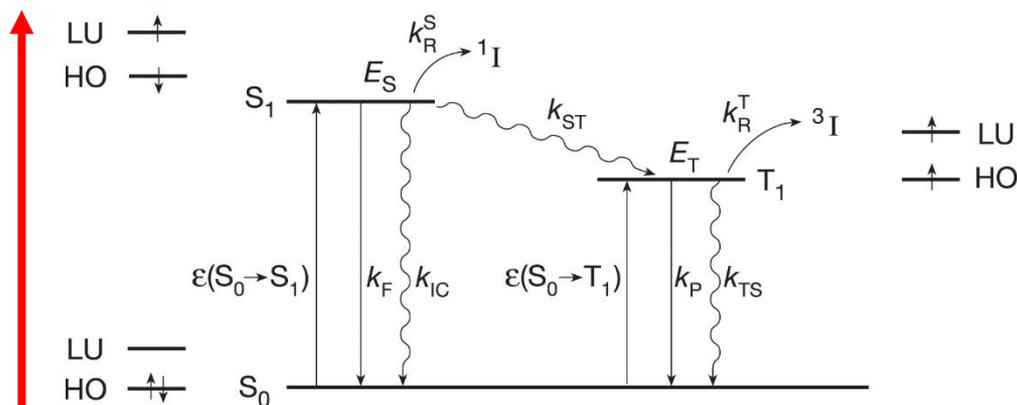
State Energy Diagrams

- Higher energy singlet (S_2, S_3 , etc.) and triplet (T_2, T_3 , etc.) states can be included, however it has been shown that excitation into these higher-energy excited states quickly deactivate back to S_1 or T_1 faster than any measurable process (**Kasha's rule**)



State Energy Diagrams

y-axis represents potential energy (PE) of the system



- While the y-axis represents the potential energy of the system, the x-axis has no physical meaning
- The lines representing the state energies for S_1 and T_1 are displaced only for convenience to avoid congestion
- A state energy diagram shows the ranking of energies of the S_0 , T_1 , and S_1 states and is most useful if actual energy values can be associated with the S_1 and T_1 states
 - How the energies of S_1 and T_1 are determined experimentally will be discussed in Chapter 4

Jablonski Diagrams

- State energy diagrams are often called **Jablonski diagrams** in honor of Aleksander Jablonski, a Polish physicist who used a schematic portrayal of the relative positions of the electronic and vibrational levels of R and *R without any attempt to indicate the relative nuclear geometries
- Note: vibrational levels have been omitted from this introduction to state energy diagrams for simplicity. These will be introduced into the state energy diagram in Chapter 2



from Wikipedia

State Energy Diagrams

- Since all of the structures in a state energy diagram have the same composition (number of atoms) and the same constitution (atom connectivity) as S_0 , but are all chemically different from S_0 , all of the states (S_0 , S_1 , T_1) are formally *isomers* of each other
- The isomerism results from differences in the *electronic configurations* (*electronic isomers*) or in the *spin configuration* (*spin isomers*) between the displayed states
- The differences in electronic isomers are due to the differences in the orbital configurations (differences in the occupancy of the HO and LU) or to differences between the electronic spin configurations of each state ($\uparrow\downarrow$ vs. $\uparrow\uparrow$)
- S_n and T_n states are spin-electronic isomers, that is, singlet spin configuration ($\uparrow\downarrow$) vs. triplet spin configuration ($\uparrow\uparrow$)
- In addition, the states in a state energy diagram may also be *stereoisomers* of one another (different spatial arrangements of the atoms)

State Energy Diagrams

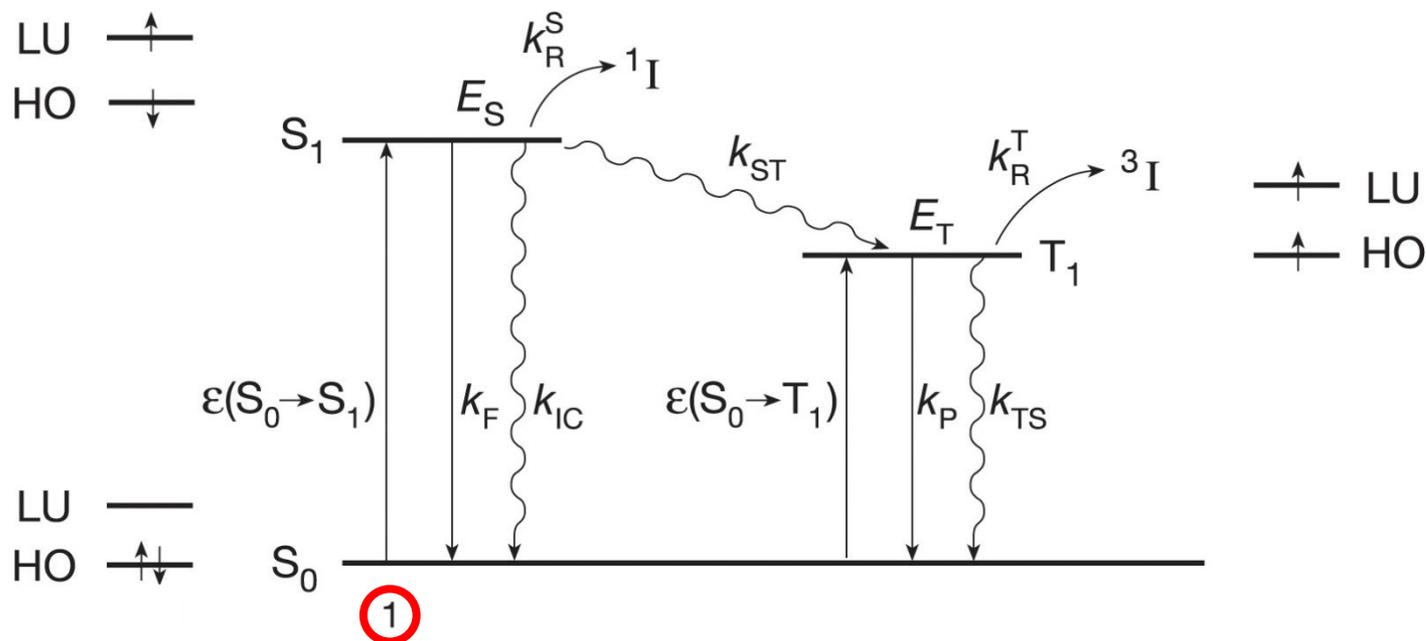
- The state energy diagram provides a useful way to organize state electronic structures, state electronic energies, and the dynamics of interstate transitions corresponding to all possible photophysical processes that interconnect S_0 , S_1 , and T_1
- Transitions between any two electronic states in the diagram correspond to the possible connection between the states indicated and can be *radiative* or *radiationless* processes
- *Photophysical processes* are defined as transitions in the energy diagram that interconvert excited states with each other or that interconvert the excited state $*R$ with the ground state R
- All possible *photophysical* transitions from S_1 and T_1 must be considered in an overall $*R \rightarrow R$ *photochemical* analysis, as *photophysical* processes will, in principle, be competitive with *photochemical* processes

State Energy Diagrams

- Let's examine the *possible* photophysical *radiative* processes in the state energy diagram, which involve the absorption or emission of a photon

- The spin-allowed singlet-singlet absorption of photons ($S_0 + h\nu \rightarrow S_1$), characterized experimentally by an extinction coefficient $\epsilon(S_0 \rightarrow S_1)$

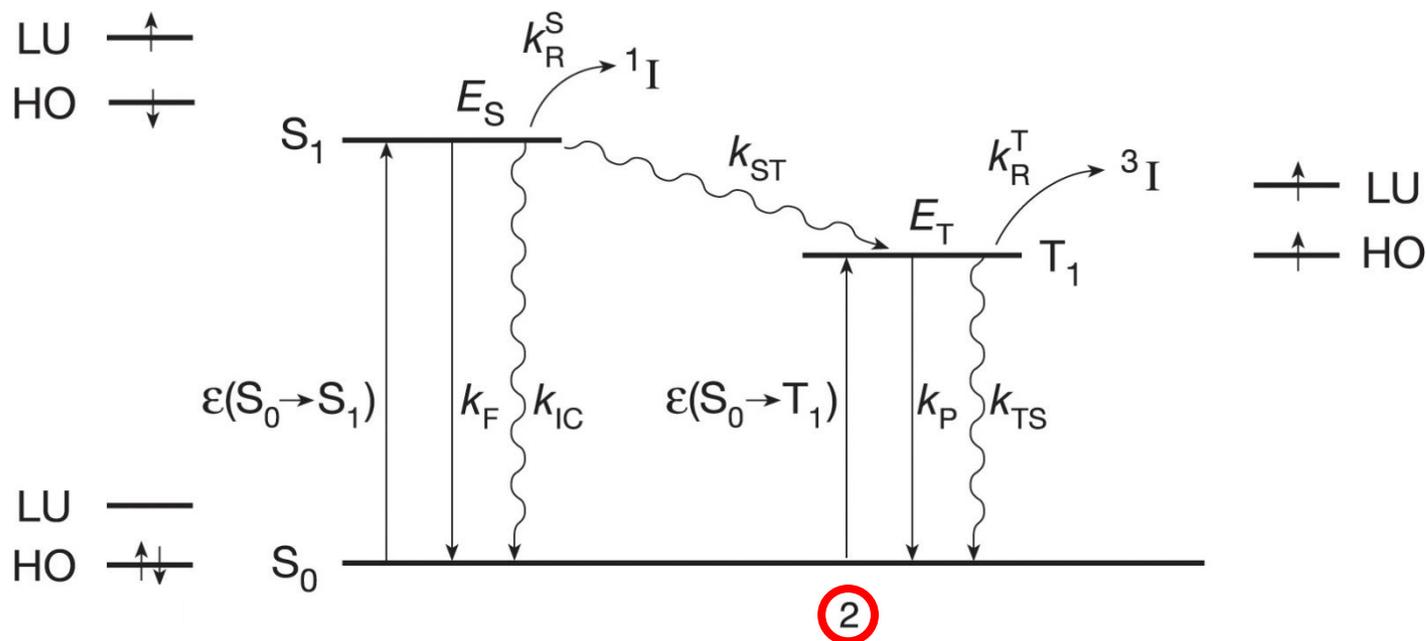
ϵ : Measurement of how strongly a chemical species absorbs light at a given wavelength (nm), per molar concentration. Units: $M^{-1}cm^{-1}$. Determined using the Beer-Lambert Law



State Energy Diagrams

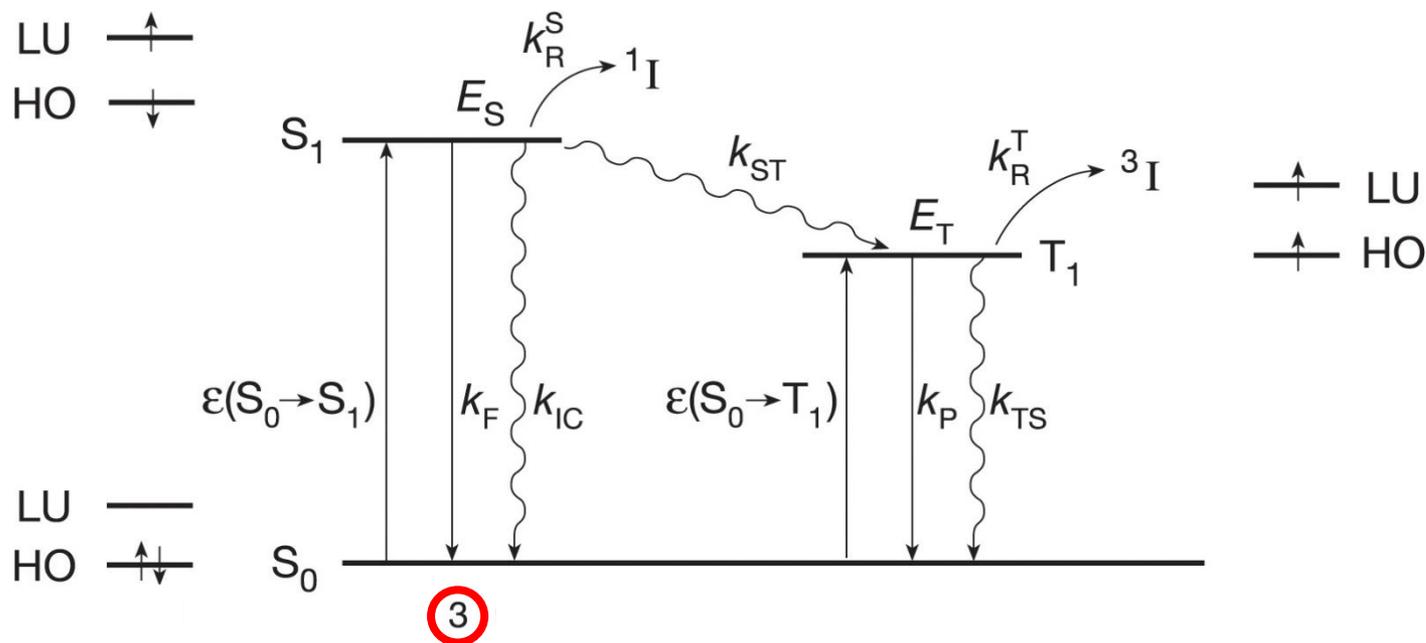
- Let's examine the *possible* photophysical *radiative* processes in the state energy diagram, which involve the absorption or emission of a photon
- 2) The spin-forbidden singlet-triplet absorption of photons ($S_0 + h\nu \rightarrow T_1$), characterized experimentally by an extinction coefficient $\varepsilon(S_0 \rightarrow T_1)$

Question: Why do we state that this process is “spin-forbidden”?



State Energy Diagrams

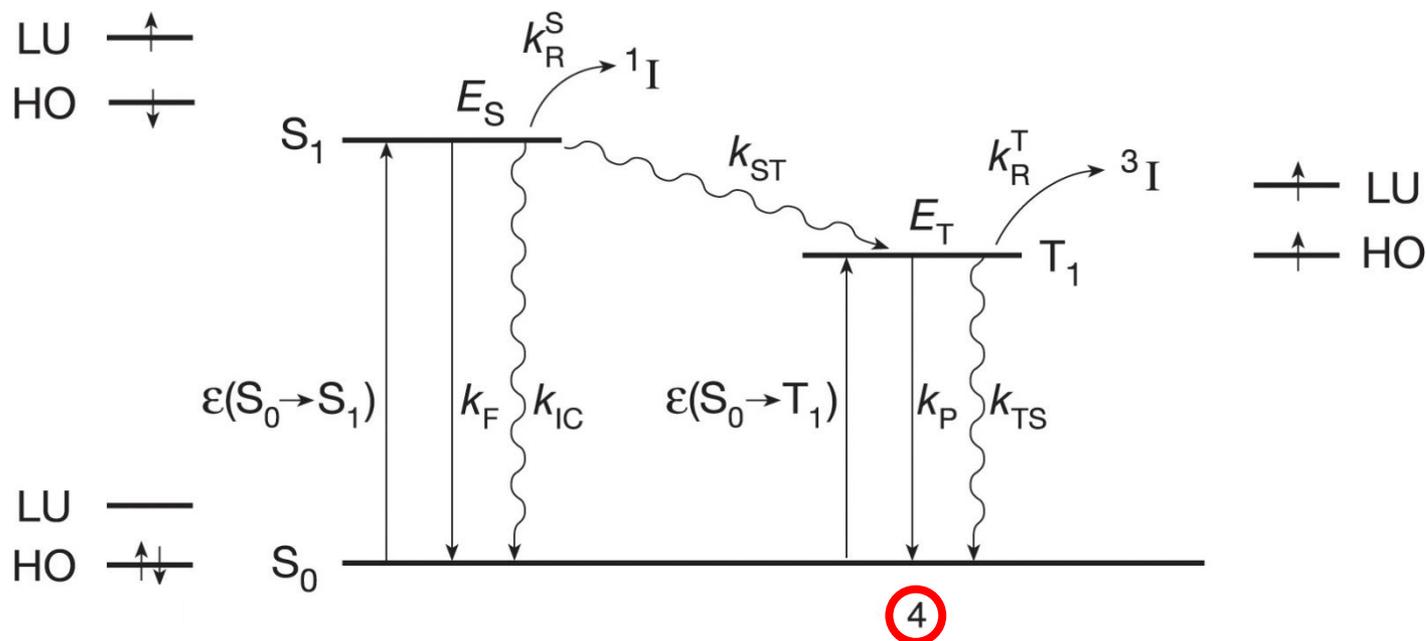
- Let's examine the *possible* photophysical *radiative* processes in the state energy diagram, which involve the absorption or emission of a photon
- 3) The spin-allowed singlet-singlet emission of photons ($S_1 \rightarrow S_0 + h\nu$), called *fluorescence*, characterized by a rate constant, k_F



State Energy Diagrams

- Let's examine the *possible* photophysical *radiative* processes in the state energy diagram, which involve the absorption or emission of a photon
- 4) The spin-forbidden singlet-triplet emission of photons ($T_1 \rightarrow S_0 + h\nu$), called *phosphorescence*, characterized by a rate constant, k_P

Important Note: At this stage, you should have noticed that solid arrows on the diagram represent *radiative* processes

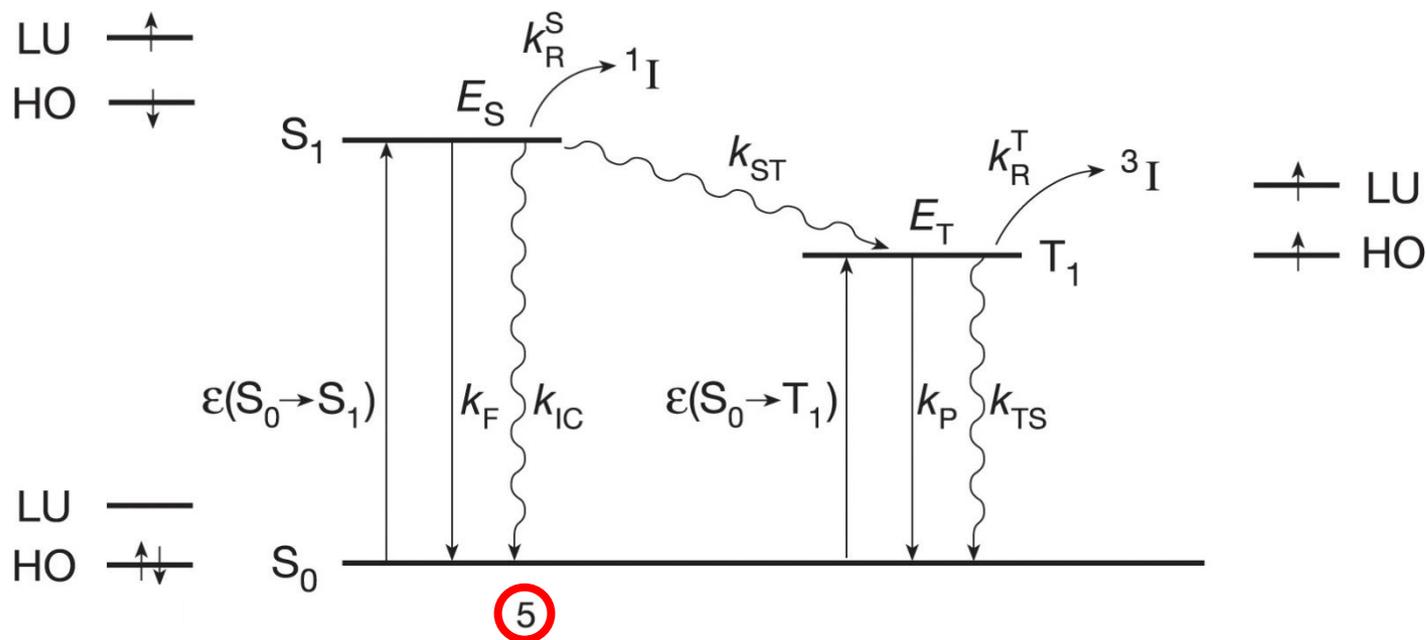


State Energy Diagrams

- Now let's examine the *plausible* photophysical *radiationless* processes in the state energy diagram

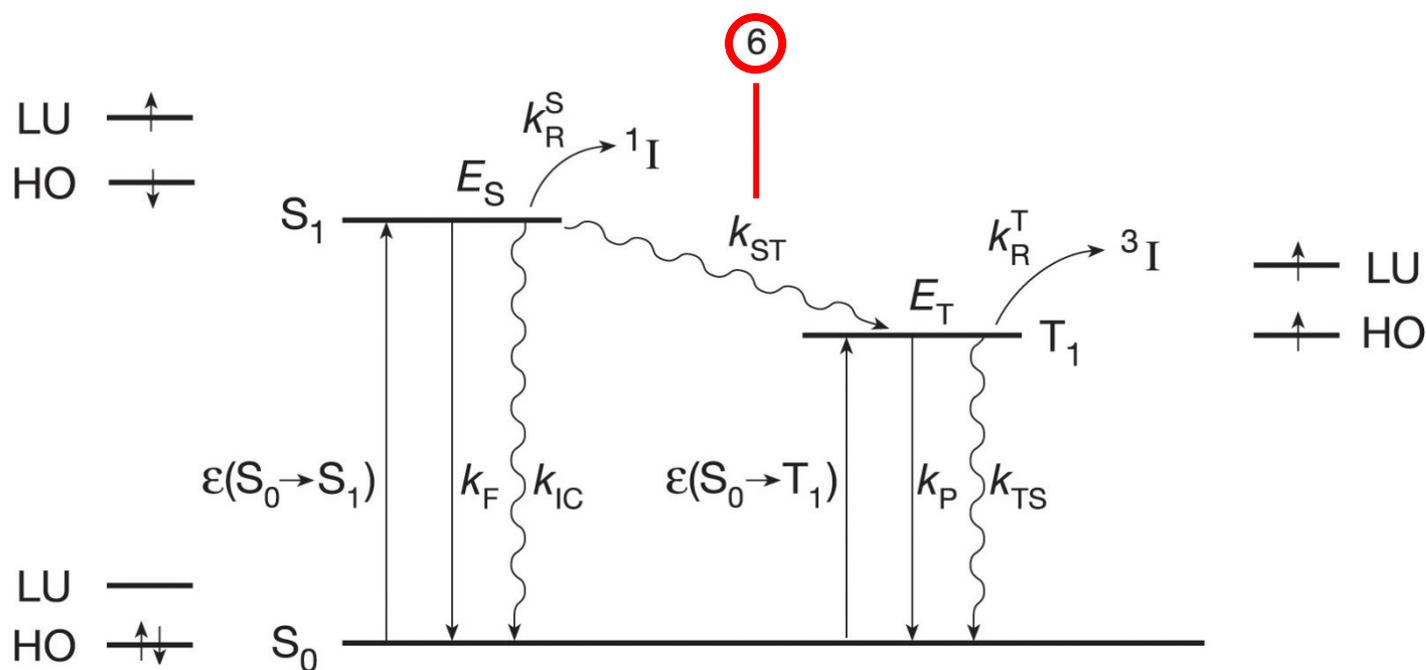
- 5) The spin-allowed radiationless transitions between the states of the same spin ($S_1 \rightarrow S_0 + \text{heat}$), called *internal conversion*, characterized by a rate constant, k_{IC}

Important Note: Radiationless processes are displayed on the diagram using wavy arrows



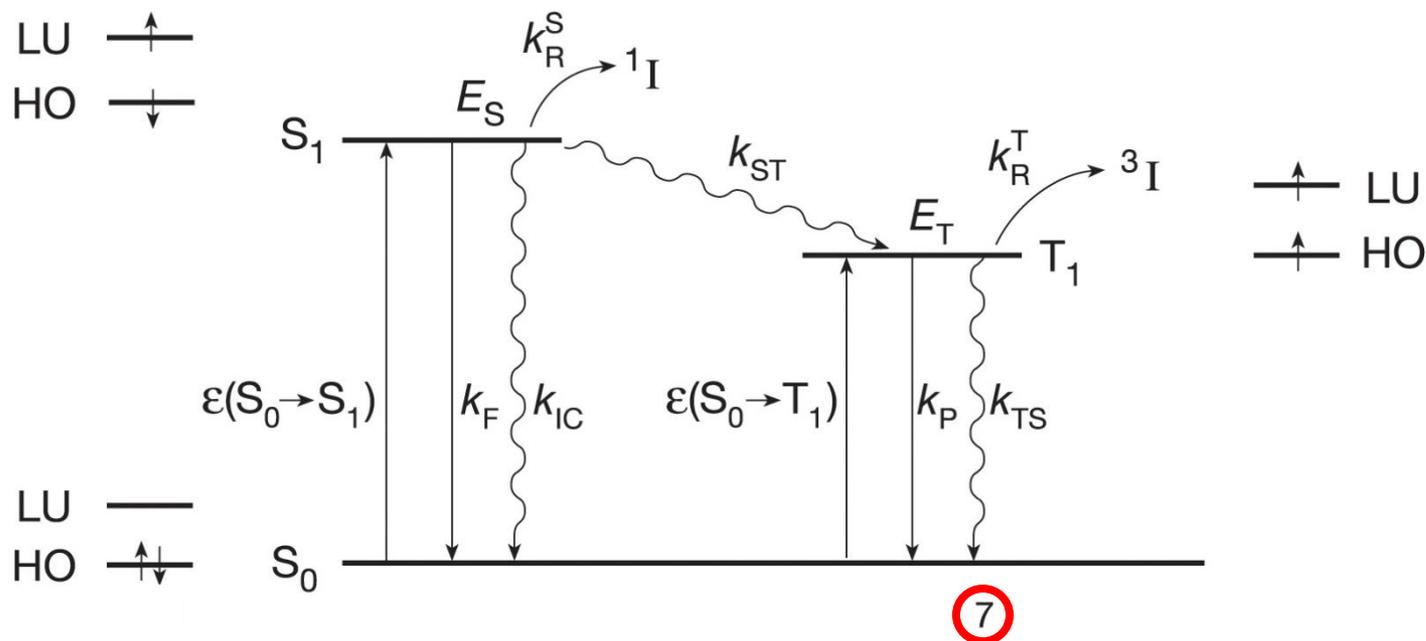
State Energy Diagrams

- Now let's examine the *plausible* photophysical *radiationless* processes in the state energy diagram
- 6) The spin-forbidden radiationless transitions between excited states of different spin ($S_1 \rightarrow T_1 + \text{heat}$), called *intersystem crossing*, characterized by a rate constant, k_{ST}



State Energy Diagrams

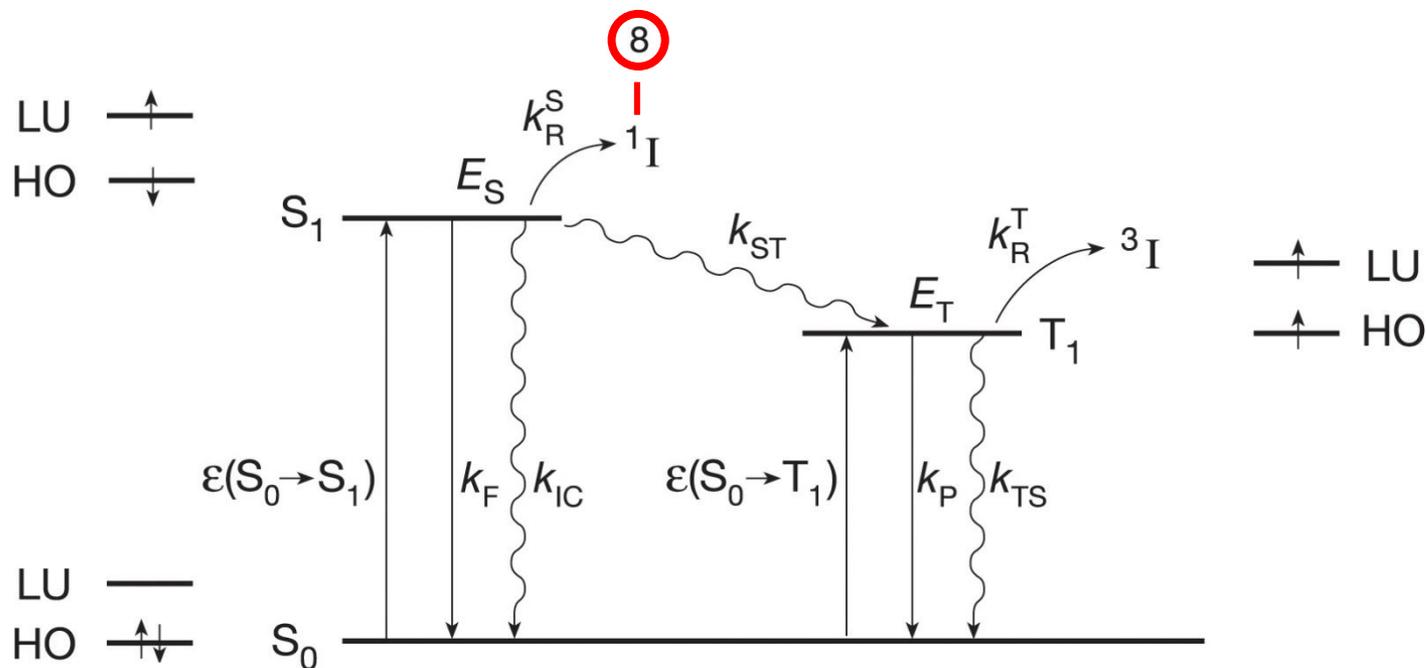
- Now let's examine the *plausible* photophysical *radiationless* processes in the state energy diagram
- 7) The spin-forbidden radiationless transitions between the triplet and the ground state ($T_1 \rightarrow S_0 + \text{heat}$), also called *intersystem crossing*, characterized by a rate constant, k_{TS}



State Energy Diagrams

- *Primary photochemical processes* can be defined as transitions from an electronically excited state that yield molecular structures of different constitution or geometry (reactive intermediates I from the prior schemes)

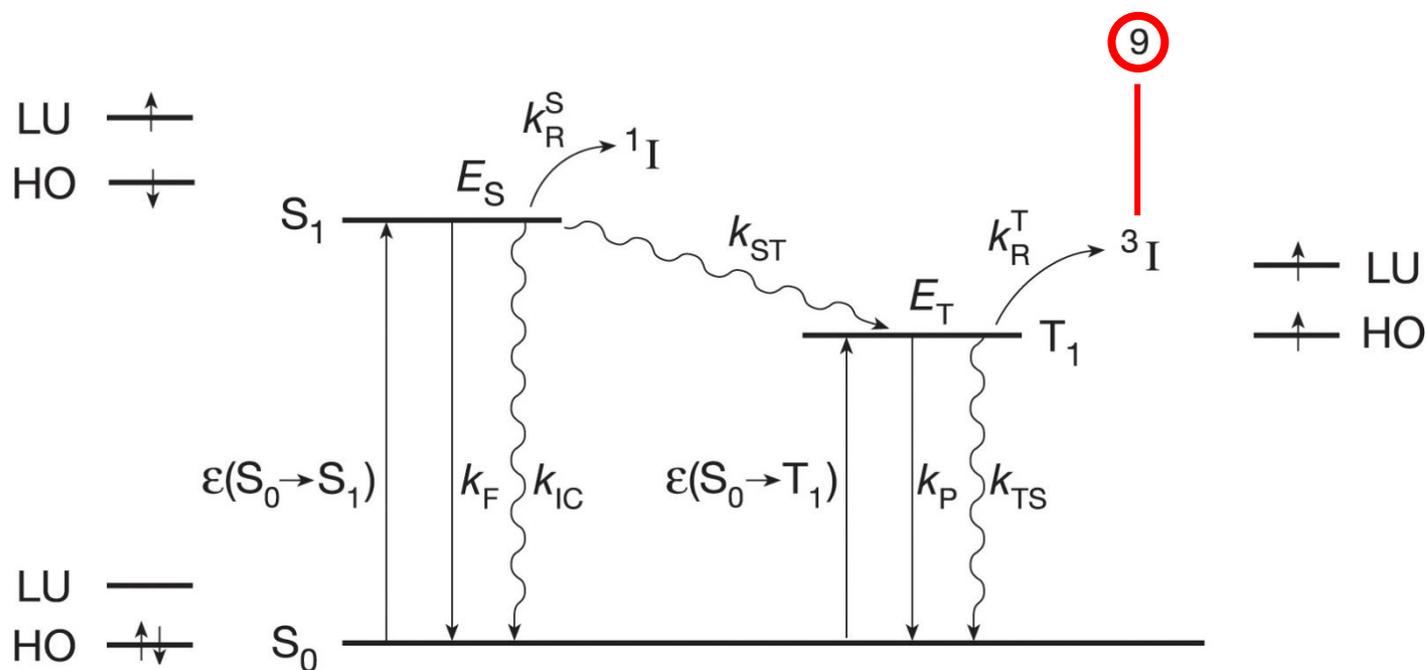
8) A photochemical reaction from S_1 to produce a reactive intermediate, $S_1 \rightarrow I$, called a *primary photochemical reaction*, characterized by a rate constant, k_R^S



State Energy Diagrams

- *Primary photochemical processes* can be defined as transitions from an electronically excited state that yield molecular structures of different constitution or geometry (reactive intermediates I from the prior schemes)

9) A photochemical reaction from T_1 to produce a reactive intermediate, $T_1 \rightarrow I$, also called a **primary photochemical reaction**, characterized by a rate constant, k_R^T



State Energy Diagrams

- In order to determine which of the *plausible* processes are most *probable* from S_1 or T_1 , we need information of the relative rates of all of the plausible photochemical and photophysical processes that compete for deactivation of these states
- The values of these rates are available if the *rate constants* (k) of the various processes are known or can be estimated via experiment or computations
- The relative rates of the transitions from a given state determine the *probability* of the various *plausible* processes that can occur from each state
- The relative rates depend on a number of structural and energetic factors that will be discussed in later chapters

Calibration Points and Numerical Benchmarks for Molecular Energetics

- Organic chemists are accustomed to counting molecules and using the mole and Avogadro's number (6.02×10^{23}) as a benchmark for the number of molecules in 1 mole of molecules
- Photochemists, however, are interested in counting not only molecules but also the number of photons in a light source
 - The intensity of the light source is the number of photons emitted per second at a specific wavelength, λ
- If we consider the photon as a “massless reagent”, then the intensity of the light absorbed from a source to produce *R in a given volume is related to the concentration of R in solution
- The number of molecules of I or P produced per photon absorbed is called the *quantum yield* (Φ) of the formation of I or P

Calibration Points and Numerical Benchmarks for Molecular Energetics

Quantum yield (Φ):

For the process $R + h\nu \rightarrow {}^*R \rightarrow I \rightarrow P$,

From standard analytical techniques

$$\Phi = \frac{\text{Rate of formation of } I \text{ or } P, \text{ or rate of conversion of } R}{\text{Intensity of light, i. e. rate of light absorption}}$$

Note that the denominator refers to *absorbed* photons, not *incident* photons

Chemical systems or physical devices called actinometers allow for the determination of the number of photons absorbed

Calibration Points and Numerical Benchmarks for Molecular Energetics

- In photochemistry, we are generally concerned with the *difference in energy of the energy gap, ΔE , between states of a molecule*, rather than the absolute energy of a state

$$\Delta E = |E_2 - E_1| \text{ (The energy gap between } E_2 \text{ and } E_1\text{)}$$

- The energy required to produce an electronically excited state ($R + h\nu \rightarrow {}^*R$) is obtained by inspecting the absorption or the emission spectrum of a molecule (Chapter 4), as well as applying Einstein's *resonance condition* for the absorption of light

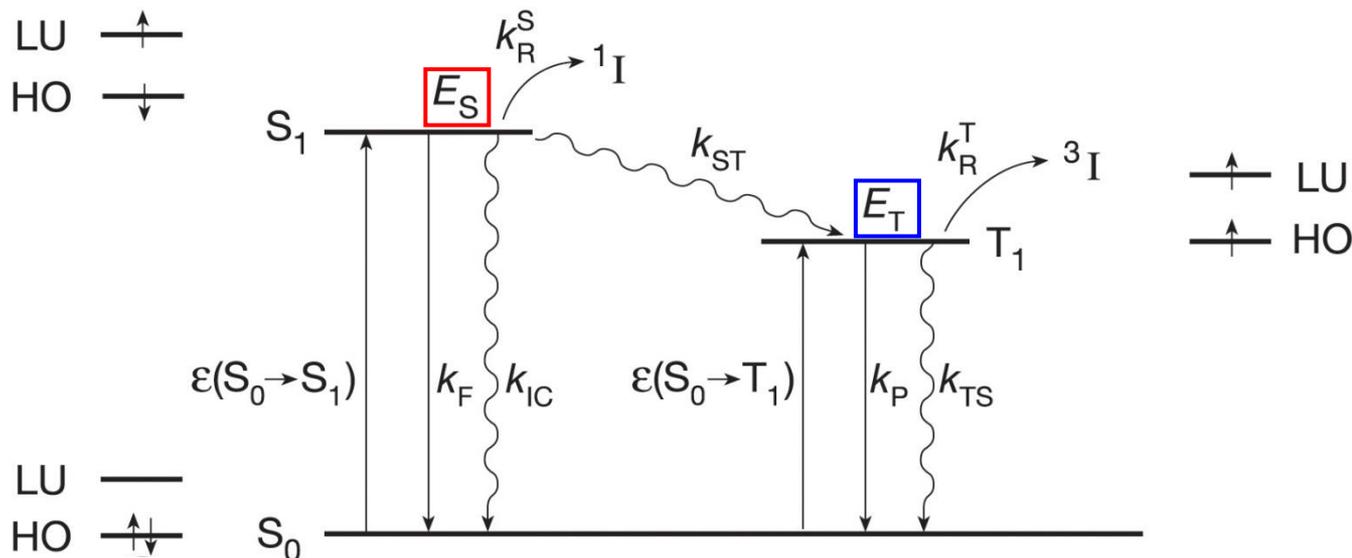
$$\Delta E = |E_2 - E_1| = |E_2({}^*R) - E_1(R)| = h\nu = hc/\lambda$$

where h = Planck's constant, ν is frequency (commonly in units of $s^{-1} = \text{Hz}$), λ is the wavelength (commonly in units of nm), c is the speed of light, and E_2 and E_1 are the energies of a molecule in an excited (*R) and initial (R) state, respectively

$$\Delta E = |E_2 - E_1| = |E_2(^*R) - E_1(R)| = h\nu = hc/\lambda$$

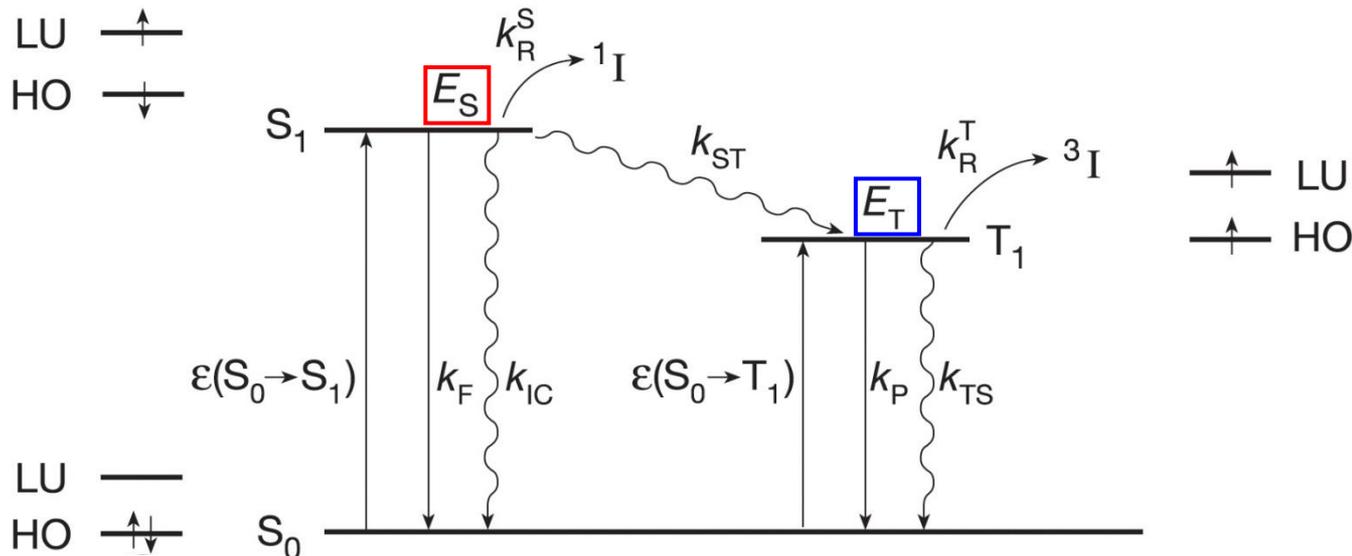
- This equation is of fundamental importance to spectroscopy and photochemistry, since it relates ΔE between two states to measurable properties, namely the frequency (ν) and wavelength (λ) of an absorbed photon
- Knowing the absolute energies (E_2 and E_1) is not required in these kinds of analyses, since *it is the difference in energy between the two states that is required when applying this equation*

Calibration Points and Numerical Benchmarks for Molecular Energetics



- In the state energy diagram, the two most important values of ΔE are the energy gap between S_1 and S_0 (called the **singlet energy**, E_S) and the energy gap between T_1 and S_0 (called the **triplet energy**, E_T)
- These energies reflect the available energy that can serve as the driving force for these two states to do work on the making and breaking of bonds in photochemical processes

Calibration Points and Numerical Benchmarks for Molecular Energetics



- Both E_S and E_T correspond to excess electronic energy that can be converted into free energy to drive bond making and breaking in photochemical processes
- We will see in Chapter 7 that the values for E_S and E_T play a critical role in photoinduced electron- and energy-transfer processes
- E_S and E_T are similarly important in overcoming thermodynamic endothermicity in bond-breaking processes

Counting Photons

- How do photochemists count the number of photons emitted from a light source or absorbed by a sample during a photoreaction?
- The equation below, the second of Einstein's light–energy relationships, relates the energy of a single photon to the wavelength (or frequency) of light

$$E = h\nu = h(c/\lambda) \quad (\text{The energy of a single photon})$$

- We can use this equation to “count” the photons emitted if we know the energy (E) of the light source
- We can also “count” the number of photons absorbed by a sample if we know the energy of light absorbed by the sample

Counting Photons

- A mole ($N_0 = 6.02 \times 10^{23}$) of photons is called an *einstein*
- The energy contained by an arbitrary number of photons or by an einstein of photons depends on the wavelength (frequency) of the corresponding light wave, which leads into the equations below where n is an arbitrary number of photons and N_0 is 1 mole of photons (or an einstein)

$$E = nh\nu = nh(c/\lambda)$$

$$E = N_0h\nu = N_0h(c/\lambda)$$

- The energy in 1 mole (N_0) of photons provides a direct relationship between the amount of light energy absorbed by the system and the number of photons absorbed

By measuring the energy of light absorbed (E) and knowing the wavelength of the absorbed light, we have a way to count photons!

Computing the Energy of a Mole of Photons

- Using the equation introduced in the previous slide, the energy of 1 mole of photons in kcal mol^{-1} may be computed from the wavelength associated with the photon

$$E(\text{kcal mol}^{-1}) = \frac{28600 \text{ kcal mol}^{-1} \text{ nm}}{\lambda (\text{nm})}$$

Remember me,
I am useful!

- The data in the Table on the next slide show how the energy of 1 mole of photons (an einstein) is related to the corresponding wavelength of light (λ , in nm)
- We will mostly use kcal mol^{-1} in this course. However, you may find the following energy conversions useful:

$$1 \text{ kcal mol}^{-1} = 4.18 \text{ kJ mol}^{-1} = 350 \text{ cm}^{-1} = 0.0434 \text{ eV}$$

Relationship among Energy and Wavelength

Type of Radiation	Wavelength (λ , nm)	Energy ($E = \text{kcal mol}^{-1}$)
Ultraviolet (UV)	200 – 400	140 – 70
Violet	~ 400	70
Green	~ 500	60
Red	~ 700	40
Near-Infrared (NIR)	~ 1000	30

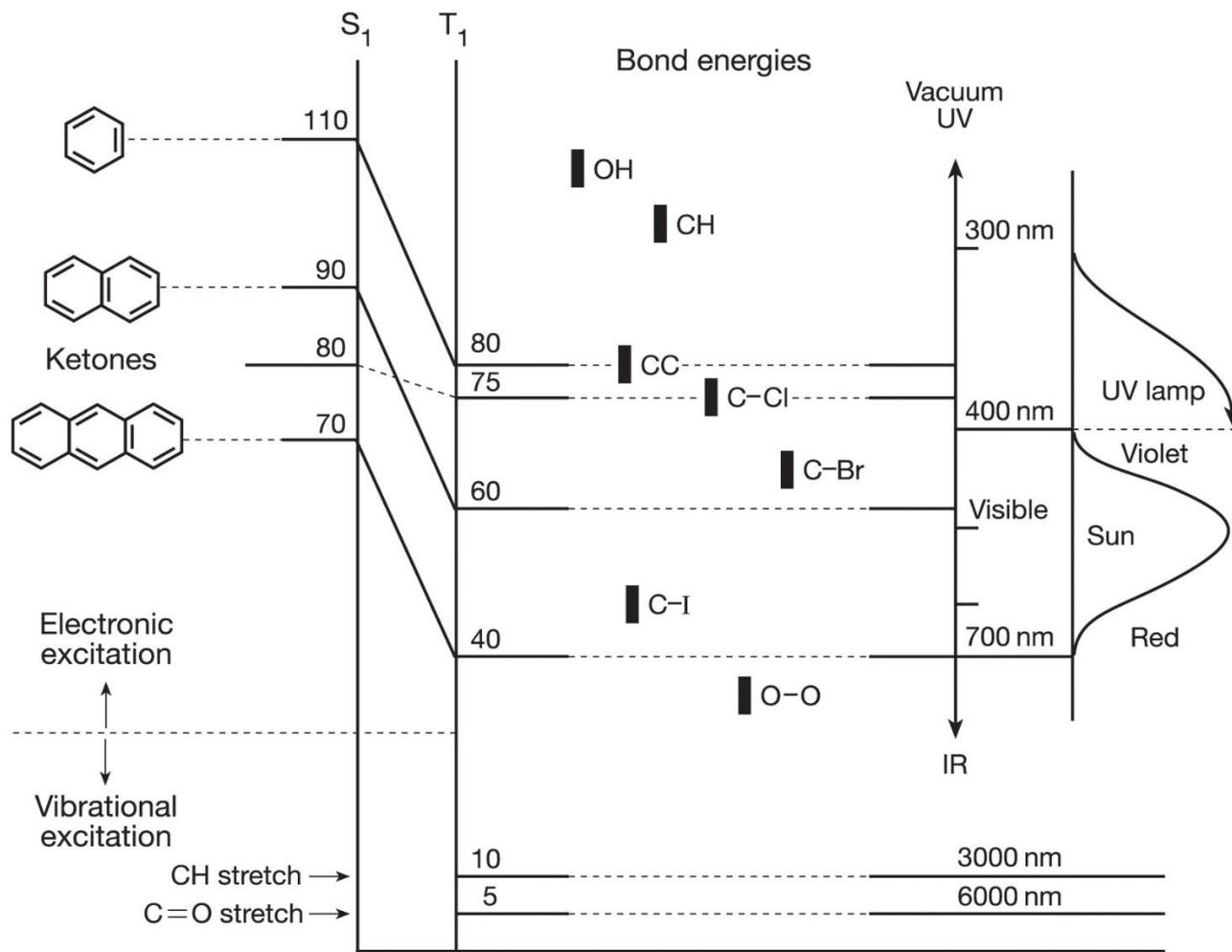
- The violet–green–red portion of the spectrum (400 – 700 nm) corresponds to the visible portion of the electromagnetic spectrum

$$E(\text{kcal mol}^{-1}) = \frac{28600 \text{ kcal mol}^{-1} \text{ nm}}{\lambda (\text{nm})}$$

Seriously,
remember me!

The Range of Photon Energies in the Electromagnetic Spectrum

- Below is a comparison of energies (in kcal mol⁻¹) involved in photochemical reactions, bond energies, and the emission of the sun



The Range of Photon Energies in the Electromagnetic Spectrum

Question: Does absorption of 250 nm light ($114 \text{ kcal mol}^{-1}$) lead to random ruptures of single bonds in organic molecules?

No!

- Only certain bonds are made or broken even when the energy per photon absorbed is higher than the energy of most of the individual bonds of a molecule
- The reasons for this selectivity include a combination of the rapid deactivation of excess vibrational energy by electronically excited states, localization of the electronic excitation on certain atoms, and the specificity with which the electronic excitation is employed to make or break bonds

The Range of Photon Energies in the Electromagnetic Spectrum

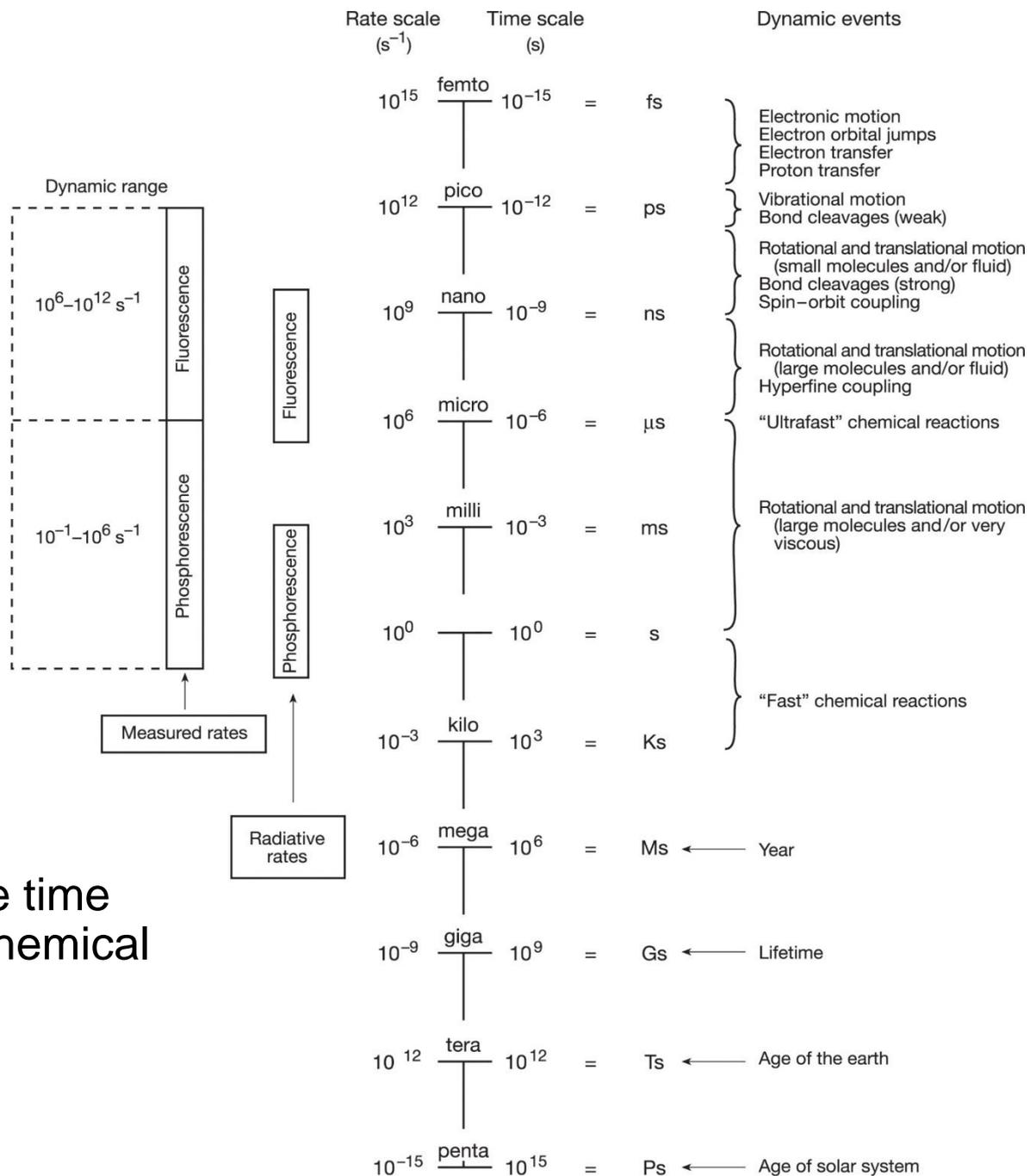
Question: Will 1 mol of photons of 350 nm light ($\sim 82 \text{ kcal mol}^{-1}$) have the same effect on a molecule as 2 mol of photons of 700 nm light (energy of 1 mol of photons is $\sim 41 \text{ kcal mol}^{-1}$, total energy also $\sim 82 \text{ kcal mol}^{-1}$)

No!

- Even if the total energy is the same, absorption of one photon of 350 nm light *instantaneously* provides a molecule with the entire 82 kcal mol^{-1} of energy
- Absorption of one photon of 700 nm light only provides 41 kcal mol^{-1} of energy
- The simultaneous absorption of two photons by a molecule using ordinary lamps is implausible
 - Having two photons and a molecule in the same space is analogous to the improbably collision or reaction of three molecules

Total energy is not as important as the energy per photon!

Time Scales



- This scheme compares the time scales of events of photochemical interest

Up Next...

**Chapter 2: Electronic, Vibrational, and Spin
Configurations of Excited States**