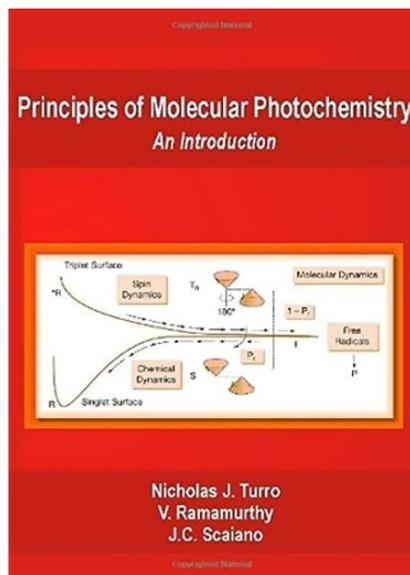
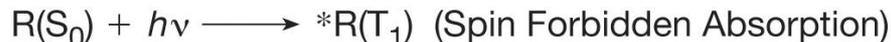
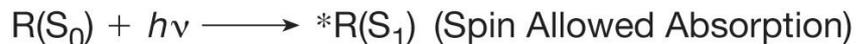
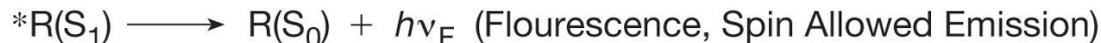
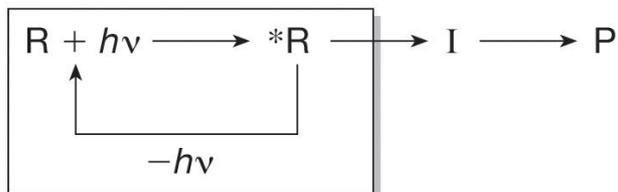


# Chapter 4: Radiative Transitions between Electronic States



# Absorption and Emission of Light

## Radiative Processes

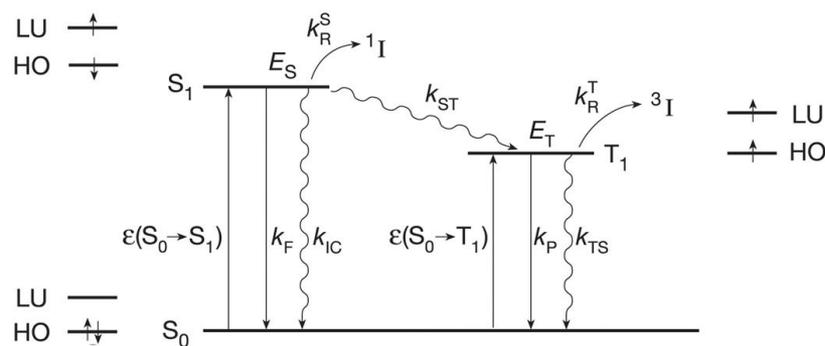


Scheme 4.1 copyright 2009 University Science Books

- In this Chapter, we are concerned with the portion of molecular organic photochemistry that involves:
  - 1) The **absorption** ( $R + h\nu \rightarrow *R$ ) of light by an organic molecule ( $R$ ) to produce an electronically excited state ( $*R$ )
  - 2) The **emission** ( $*R \rightarrow R + h\nu$ ) of light from an electronically excited state ( $*R$ ) to produce a ground state ( $R$ )
- Both spin allowed and spin forbidden transitions will be discussed

# Absorption and Emission Spectra of Organic Compounds

- Electronic absorption and emission spectra provide important information concerning the structure, energetics, and dynamics of  $^*R$ , in particular on the following parameters
  - Structures, energies, lifetimes, electron configurations, and quantum yields
- For example, from knowledge of the  $S_0 + h\nu \rightarrow S_1$  and  $S_0 + h\nu \rightarrow T_1$  absorption processes, and of the  $S_1 \rightarrow S_0 + h\nu$  and  $T_1 \rightarrow S_0 + h\nu$  emission processes, one can often construct a fairly complete state energy diagram
- From measurements of the lifetimes of  $S_1$  and  $T_1$  and the quantum efficiencies of emission  $\Phi$ , we can deduce the rate constants ( $k$ ) of radiative and radiationless photophysical pathways available to  $S_1$  and  $T_1$



# Benchmarks

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- In Chapter 1, we learned that for organic molecules the energy required to excite an electron from an occupied valence orbital ( $\sigma$ ,  $\pi$ , or  $n$ ) to an unoccupied antibonding orbital ( $\pi^*$  or  $\sigma^*$ ) corresponds to light whose wavelength is typically in the range of 200 nm (UV light, 143 kcal mol<sup>-1</sup>) to 700 nm (red light, 41 kcal mol<sup>-1</sup>)
- Saturated organic compounds (alkanes) are generally “transparent” to light in the region ~ 200 – 700 nm
- The lowest energy absorption corresponds to a HO  $\rightarrow$  LU orbital jump of an electron; for saturated hydrocarbons this jump corresponds to a  $\sigma(\text{HO}) \rightarrow \sigma^*(\text{LU})$  orbital transition
- The energy gap between  $\sigma$  and  $\sigma^*$  orbitals for saturated hydrocarbons corresponds to energies greater than that of a 200 nm photon

# Benchmarks

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- On the other hand, unsaturated organic molecules (ketones, olefins, conjugated polyenes, enones, aromatic hydrocarbons, etc.) possess several absorption bands in the conventional “photochemical” region of the electromagnetic spectrum, 250 – 700 nm
- The longer wavelength limit is set by considerations of the minimum energy required to excite electrons (light of wavelengths < 700 nm)
- Wavelengths in the range of 700 – 10,000 nm corresponds to near-IR and IR
- The energy of photons corresponding to these wavelengths is generally too small to excite electrons from a HO to a LU

# Benchmarks

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- A **chromophore** (“color bearer”) is defined as an atom or group of atoms that behave as a unit in light absorption
- A **lumophore** (“light bearer”) is an atom or group of atoms that behave as a unit in light emission (fluorescence or phosphorescence)
- Typically, organic **chromophores** and **lumophores** are common organic functional groups, such as:
  - ketones ( $\text{C}=\text{O}$ )
  - olefins ( $\text{C}=\text{C}$ )
  - conjugated polyenes ( $\text{C}=\text{C}-\text{C}=\text{C}$ )
  - conjugated enones ( $\text{C}=\text{C}-\text{C}=\text{O}$ )
  - aromatic compounds

# Benchmarks

- The table below lists some numerical benchmarks for the maximum of the longest wavelength absorption band ( $\lambda_{\max}$ ) and the extinction coefficient of absorption ( $\epsilon_{\max}$ ) of some common organic chromophores
- Transitions listed generally correspond to lowest energy (longest wavelength) electronic HO  $\rightarrow$  LU orbital transition of the chromophore

Chromophore	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ (cm <sup>-1</sup> M <sup>-1</sup> )	Transition Type
C-C	<180	1,000	$\sigma, \sigma^*$
C-H	<180	1,000	$\sigma, \sigma^*$
C=C	180	10,000	$\pi, \pi^*$
C=C-C=C	220	20,000	$\pi, \pi^*$
Benzene	260	200	$\pi, \pi^*$
Naphthalene	310	200	$\pi, \pi^*$
Anthracene	380	10,000	$\pi, \pi^*$
C=O	280	20	$n, \pi^*$
N=N	350	100	$n, \pi^*$
N=O	660	200	$n, \pi^*$
C=C-C=O	350	30	$n, \pi^*$
C=C-C=O	220	20,000	$\pi, \pi^*$

# Benchmarks

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- The data in the Table on the previous slide show that the wavelength ( $\lambda$ ) or corresponding frequency ( $\nu$ ) of absorption maxima vary greatly with the chromophore structure, as does the strength of the absorption as measured by  $\epsilon_{\max}$
- *Note that absorptions in the Table correspond to spin-allowed singlet-singlet transitions*
- The values of  $\epsilon_{\max}$  for spin-forbidden, singlet-triplet transitions are usually  $\ll 1 \text{ cm}^{-1} \text{ M}^{-1}$ , so that a sample is effectively transparent at wavelengths corresponding to the transition

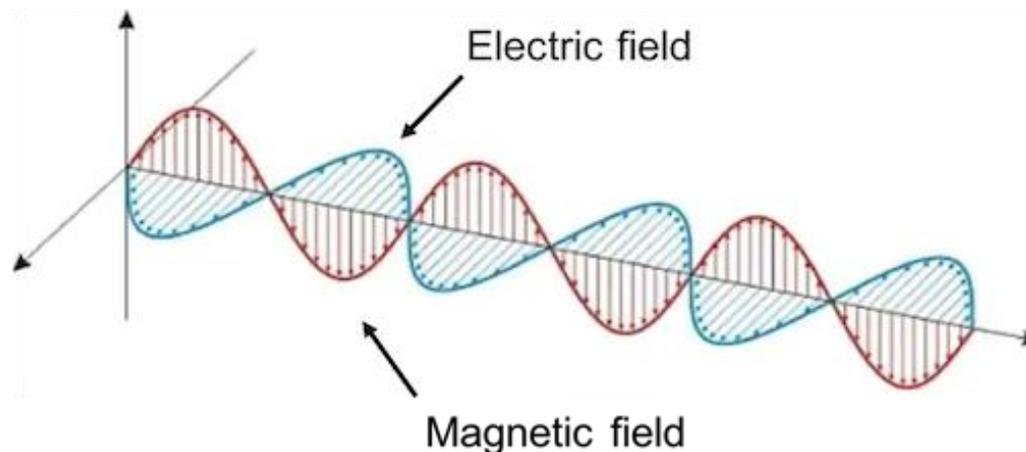
# A Pictorial Representation for the Absorption of Light

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- Photons are viewed as particles that allow the exchange in energy between the electric portion of the electromagnetic field and the electrons of a molecule under the rule of quantum mechanics
- The most important interaction between the electromagnetic field and the electrons of a molecule can be modeled as the interaction of two oscillating electric dipole systems: *the oscillating electromagnetic field that fills the entire universe and the oscillating electrons that are fixed to the nuclear framework of a molecule in matter*
- The two oscillating electric systems, when coupled to one another, behave as a reciprocally interacting and coupled system of PE donor and acceptor attempting to participate in a common resonance if a common frequency ( $\nu$ ) is found

# A Pictorial Representation for the Absorption of Light

- The electromagnetic field is visualized as a field of electric dipoles that pervade the universe and oscillate at a range of frequencies ( $\nu$ )
- If the electrons of a molecule possess a resonance oscillation frequency ( $\nu$ ) that corresponds to a resonance oscillation frequency ( $\nu$ ) of one of the oscillating dipoles (photons) in the available electromagnetic field, and if the electrons and the field are coupled by a significant dipole-dipole interaction, the electromagnetic field can interact with the electrons and exchange energy with the electrons by driving the electrons into oscillation and result in the absorption of photons from the electromagnetic field



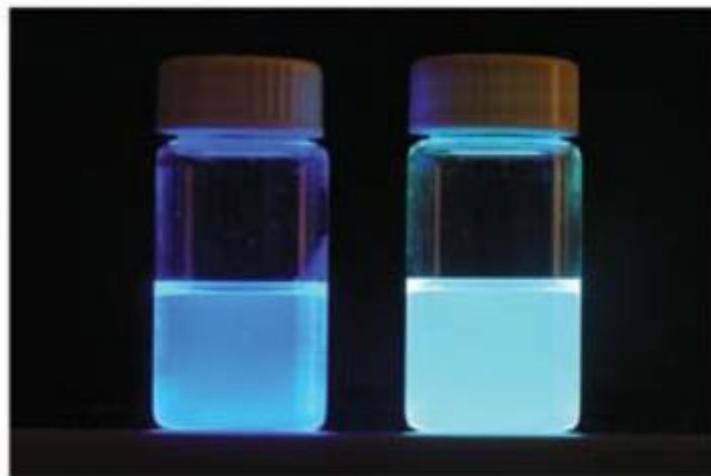
# A Pictorial Representation for the Absorption of Light

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- The interactions are completely analogous to that of two interacting antennae, one an energy transmitter and the other an energy acceptor
- The dipole-dipole interaction can cause a coupling of the two antennae (i.e., a resonance results between the two antennae)
- This resonance is most efficient when there exists a frequency ( $\nu$ ) that is common to both the electromagnetic field and the electronic transition for the photon ( $E = h\nu$ ) and the energy gap for the transition of the electron from one state to the other ( $\Delta E = h\nu$ )
- At a special resonance frequency ( $\nu$ ) corresponding to  $\Delta E = h\nu$ , the electrons of a molecule (R) can **absorb** energy from the electromagnetic field (by **absorbing** a photon)
- The electromagnetic field is then impoverished by one photon, and an excited oscillating electron of a molecule takes all the energy from the photon and becomes an electronically excited molecule (\*R)

# A Pictorial Representation for the Absorption of Light

- **Emission** is viewed as the reverse process, in which an excited oscillating electron interacts with the electromagnetic field and the electromagnetic field becomes excited by the photon emitted by the molecule ( $*R$ )
- The photon is transferred from the oscillating electron of the excited molecule to the electromagnetic field; the field's energy is increased by the energy of one more photon and an electron of the molecule returns from an excited state ( $*R$ ) to its ground state ( $R$ )



# Interaction of Electrons with the Electric and Magnetic Forces of Light

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- The absorption or emission of light, as for all transitions of molecules, requires the conservation of energy
- When two electronic states separated by an energy,  $\Delta E = E_1 - E_2$ , are coupled by some interaction, the electron density appears to oscillate and vary with time
- From the Einstein resonance relation (eq 1a), an energy separation of  $E_1 - E_2$  corresponds to the frequency of oscillation (eq 1b)

$$\Delta E = E_1 - E_2 = h\nu \quad (1a)$$

$$\nu = (E_1 - E_2)/h \quad (1b)$$

Resonance condition for the absorption or emission of light

# Interaction of Electrons with the Electric and Magnetic Forces of Light

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- A key to understanding the interaction of light with organic molecules is that electrons can be set into resonant oscillation (resonance) by the oscillating dipolar electric field of light only when eq 1 is obeyed
- Under the condition of resonance, an electron (of R) may absorb energy from the electromagnetic field set up by the light wave, or an electron of \*R may emit a photon as electromagnetic radiation

# Interaction of Electrons with the Electric and Magnetic Forces of Light

- An electromagnetic wave exerts both electric and magnetic forces on charged particles (e.g., electrons and nuclei) and on magnetic dipoles (e.g., the magnetic moments associated with electron and nuclear spins)
- We can view light as mapping oscillating dipolar electric and magnetic force fields into the neighborhood of space about its direction of propagation

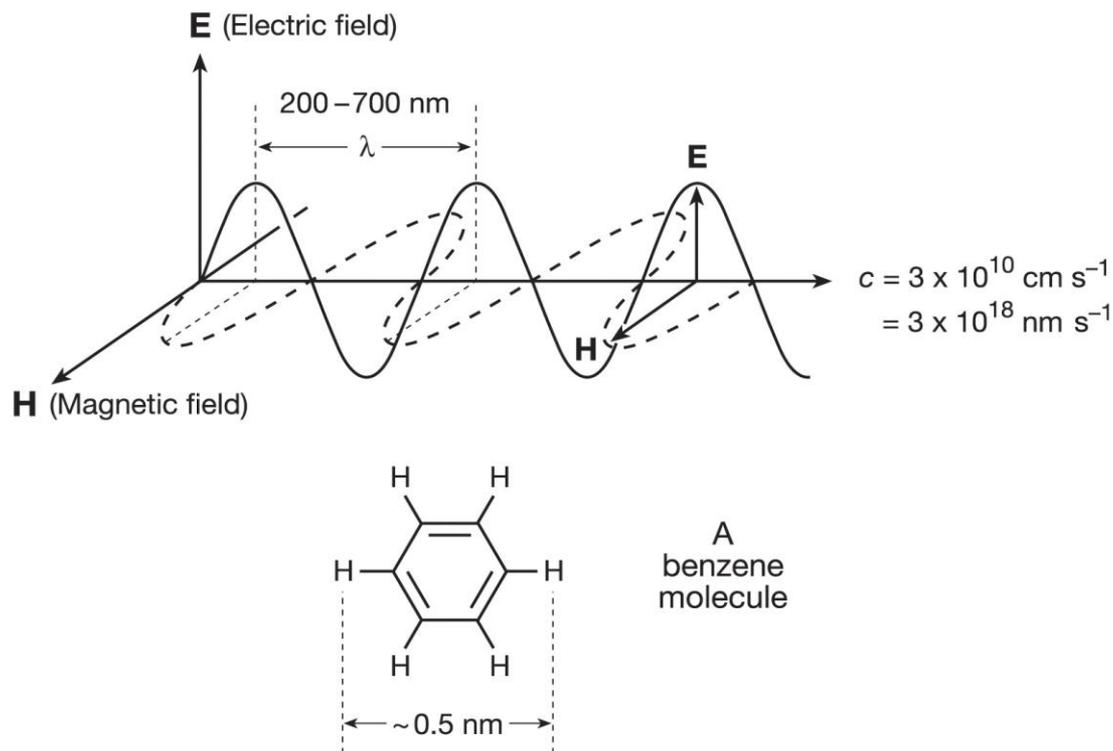


Figure 4.3 copyright 2009 University Science Books

# Photons as Massless Reagents

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- Like the molecules of an organic reagent, which can be counted, we can also count photons
- A source of light frequency  $\nu$  can be regarded as being composed of  $N$  photons, each of which possesses the energy  $h\nu$
- Each photon of wavelength  $\lambda = c/\nu$  carries an energy  $h\nu$  and a linear momentum  $h\nu/c$

Low-frequency (long-wavelength) photons carry little energy and momentum; high-frequency (short-wavelength) photons carry a great deal of both energy and momentum

# Photons as Massless Reagents

- Eq 2 provides a quantitative connection between the energy ( $E$ ) for Avogadro's number ( $N_0$ ) of photons with a light source of frequency  $\nu$  (wavelength  $\lambda$ )

$$E = N_0 h \nu = N_0 h (c/\lambda) \quad (2)$$

- From eq 2, we can construct the following Table to describe the relationship between the number of photons ( $N$ ) that corresponds to 100 kcal mol<sup>-1</sup> of energy

Spectra Region	$\lambda$ (nm)	$\nu$ (s <sup>-1</sup> )	einsteins ( $N$ )
Gamma	0.001	$1.0 \times 10^{20}$	$3.5 \times 10^{-6}$
X Ray	0.1	$1.0 \times 10^{18}$	$3.5 \times 10^{-4}$
UV	300	$1.0 \times 10^{15}$	1.1
Violet	400	$7.5 \times 10^{14}$	1.5
Green	500	$6.0 \times 10^{14}$	1.8
Red	700	$4.3 \times 10^{14}$	2.5
NIR	1000	$3.0 \times 10^{14}$	3.5
IR	5000	$0.6 \times 10^{14}$	17.3
Microwave	$10^7$	$3.0 \times 10^{10}$	$3.3 \times 10^4$
Radiowave	$10^{11}$	$3.0 \times 10^6$	$3.3 \times 10^7$

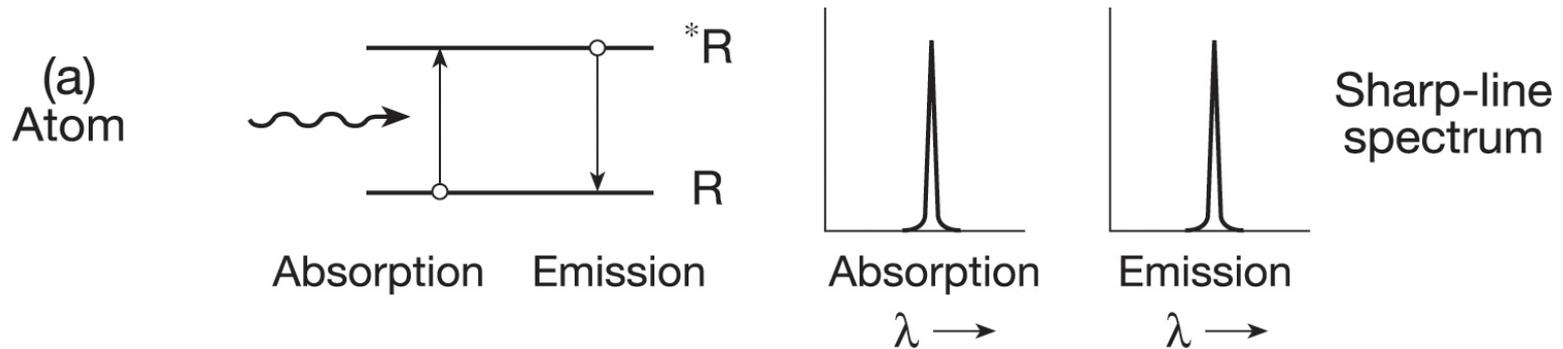
# Photons as Massless Reagents

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- It is very important in photochemistry to understand the difference between the energy and intensity of photons
- The intensity of a beam of monochromatic light of frequency  $\nu$  refers to the number of photons in the beam
- The greater the intensity of a beam of monochromatic light, the greater the number of photons in the beam
- No matter what the intensity of the beam, each photon carries the energy  $E = h\nu$
- Therefore, a weak light beam of high frequency (short-wavelength) may possess sufficient energy to break strong bonds, whereas a strong beam of low frequency may not be able to break even weak bonds

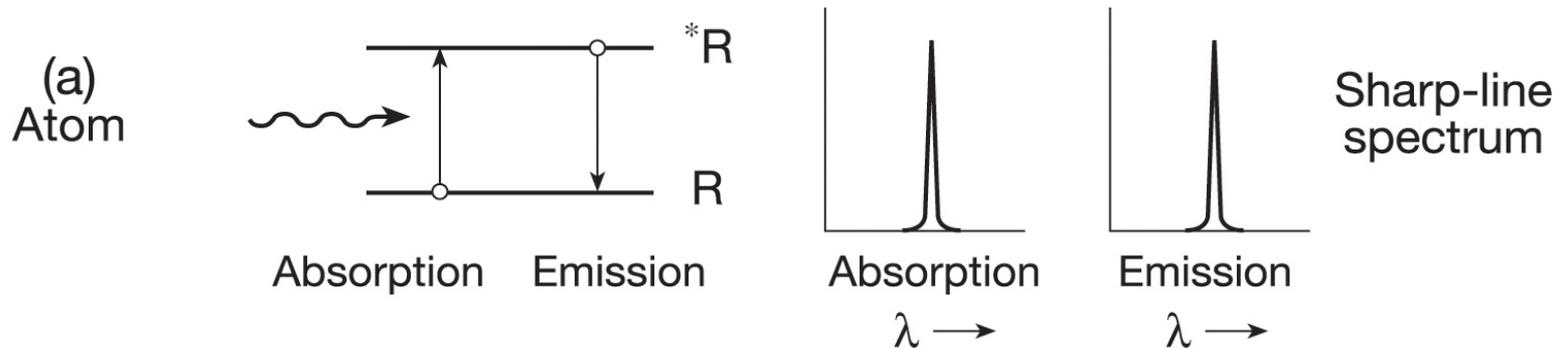
# The Shapes of Absorption and Emission Spectra

- Let's qualitatively examine the shape of the bands in an absorption or emission spectrum
- Let the energy of the ground state R be  $E$  and the energy of the excited state  $^*R$  be  $^*E$
- The resonance equation  $\Delta E = h\nu$  then corresponds to the transitions between the two energy levels,  $E$  and  $^*E$ , with an energy gap  $\Delta E = ^*E - E$
- We might expect that the absorption and emission spectra we observe are "sharp lines" with respect to the frequency  $\nu$  of the absorbed or emitted light
- In fact, only the absorption and emission spectra of atoms are close to being sharp lines



# The Shapes of Absorption and Emission Spectra

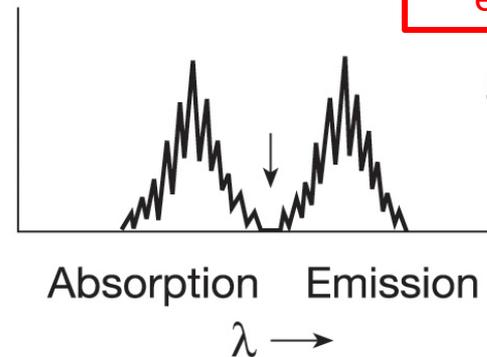
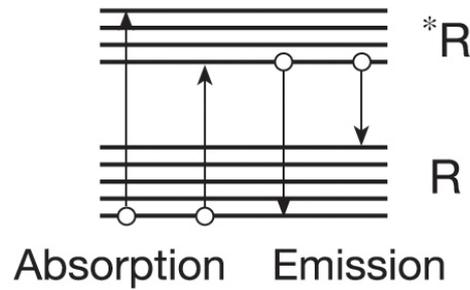
- This sharpness of an atomic spectrum appears because the energies  $E$  and  $*E$  of the electronic states of atoms can be accurately described by specifying the electronic energies of the electronic orbitals
- At low pressures in the gas phase for an atom, there are no rotations, vibrations, or collisions that “broaden” the values of  $E$  and  $*E$
- Since  $E$  and  $*E$  are sharply defined, the value of  $\Delta E = h\nu$  is sharply defined, leading to sharp lines in the absorption and emission spectra



# The Shapes of Absorption and Emission Spectra

- For a molecule, because of coupling between the electrons and vibrations, the transitions between R and  $*R$  are not “pure” electronic transitions, but rather are “vibronic” transitions that can possess a range of energies
- In order to describe the electronic states of a molecule, one must consider not only the motions of the electrons but also the motions of the nuclei relative to one another and the molecules as a whole (e.g., vibrations and rotations)
- As a result, the absorption (and emission) spectrum for a  $HO \rightarrow LU$  of a molecule may involve many vibrational transitions over a range of energies corresponding to slightly different conformations of R and  $*R$ , even in the gas phase at low pressures

(b)  
Molecule  
with distinct  
substates



Termed absorption and  
emission “bands”

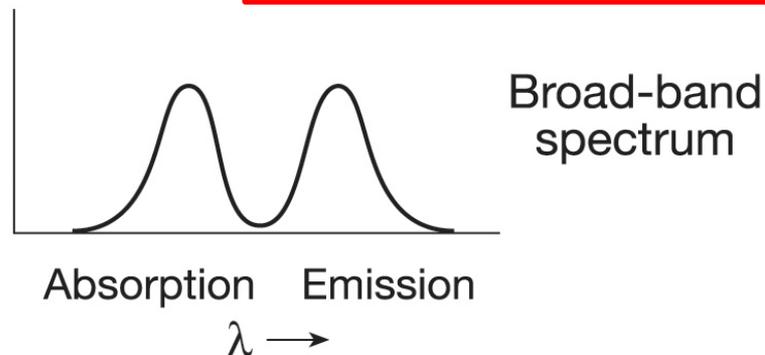
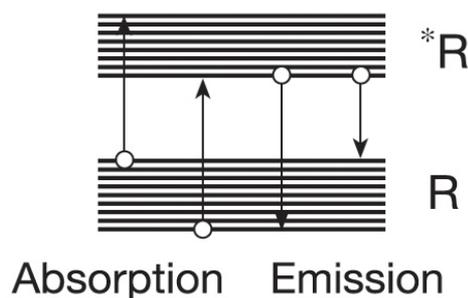
Spectrum with  
vibrational  
structure

# The Shapes of Absorption and Emission Spectra

- For organic molecules in solution, the situation is even more complex
- In solution, R and \*R are surrounded by solvent molecules that may be instantaneously intermolecularly oriented about R and \*R in many different supramolecular configurations; in addition, vibrations are coupled to within the molecule and to some extent to the solvent molecules
  - Described as R@solvent
- Each of these configurations for the R@solvent +  $h\nu \rightarrow$  \*R@solvent transitions will have a slightly different energy gap for absorption or emission, leading to a broadened molecule spectrum where the molecular vibrational structure is blurred out or lost completely

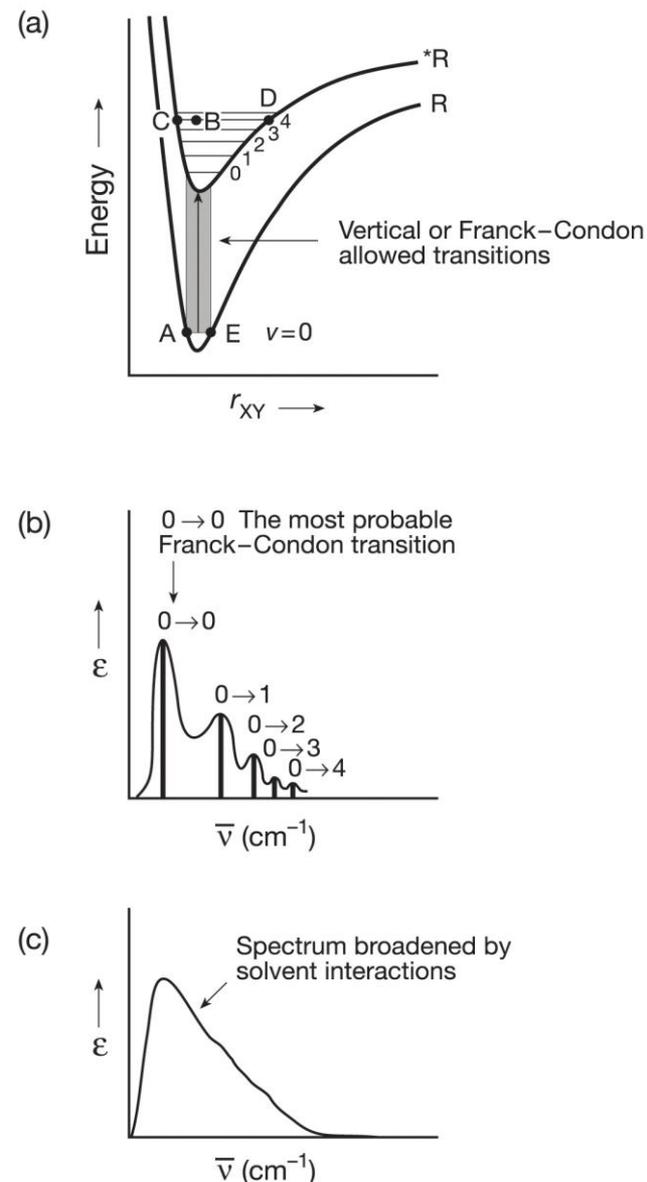
Termed as “featureless bands”  
with a single maximum

(c)  
Molecule  
with many  
unresolved  
substates



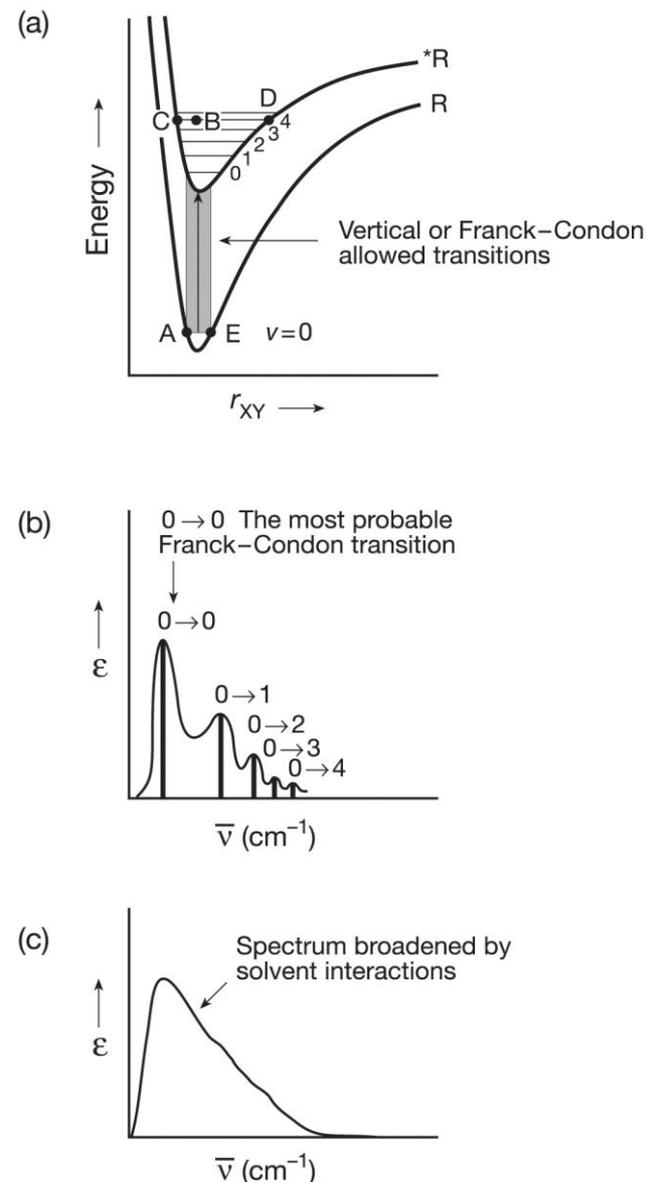
# Absorption Spectra of Organic Molecules

- The **Franck–Condon principle** leads to the conclusion that there will be a difference in probability of vibrational transitions between the wave functions corresponding to the R and \*R states
- Let's examine the role of the FC principle in terms of the semiclassical model, where the vibrations are quantized but vibrational wave functions aren't considered explicitly
- Here we have situation where the two potential curves for R and \*R are displaced vertically, and the equilibrium separation ( $r_{eq}$ ) is the same
- As a result, the equilibrium geometries of R and \*R should be similar



# Absorption Spectra of Organic Molecules

- Since the FC principle requires absorption to occur vertically, a relatively strong  $v = 0 \rightarrow v = 0$  transition (termed  $0 \rightarrow 0$  band) is observed for both absorption and emission, and the  $0 \rightarrow 0$  band of the absorption and emission spectra overlap significantly
- The molecule undergoes zero-point vibrational motion ( $v = 0$ ) between points A and E
- A vertical transition to point B ( $v = 4$ ) is **Franck–Condon forbidden**, as well as to points C and D
- As a result, the  $0 \rightarrow 4$  transition is very weak



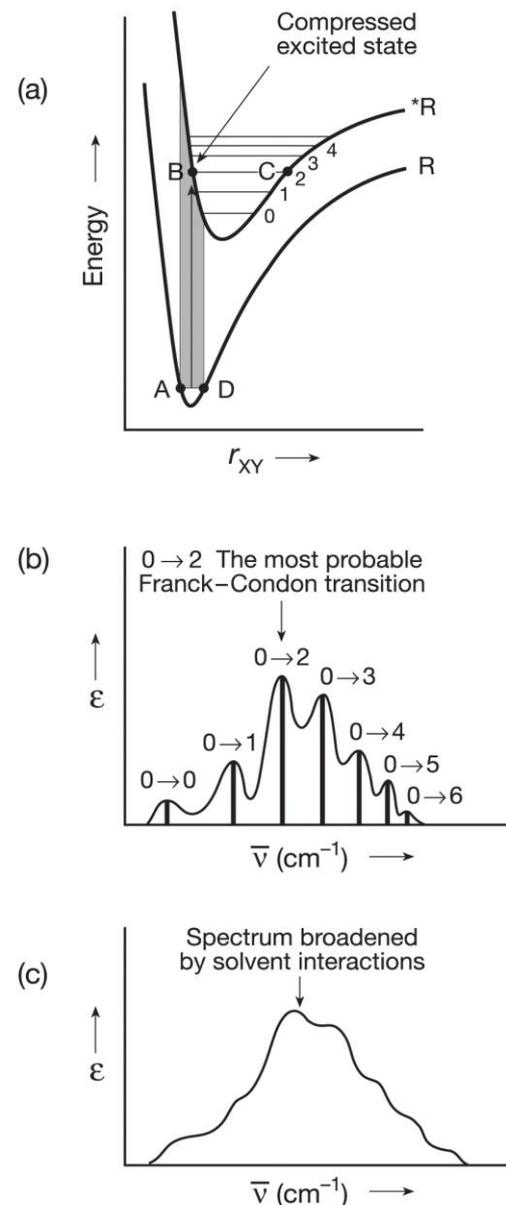


# Absorption Spectra of Organic Molecules

- The next two slides represent situations where the excited curve minima for  $^*R$  are significantly displaced relative to  $R$

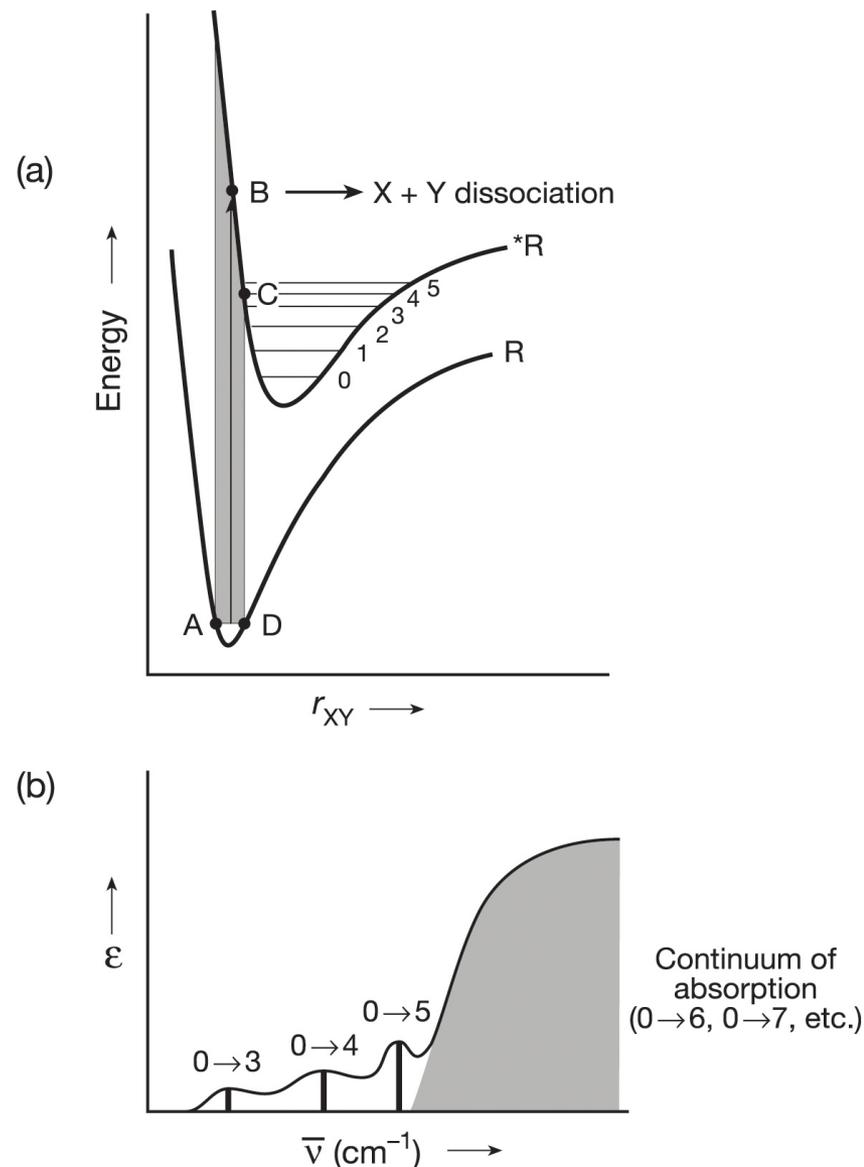
$r_{eq}$  is assumed to be larger for  $^*R$  compared to  $R$ . Do you remember why?

- In this example, the  $0 \rightarrow 2$  and  $0 \rightarrow 3$  vibrational bands are relatively intense, and the  $0 \rightarrow 0$  and  $0 \rightarrow 1$  bands are relatively weak



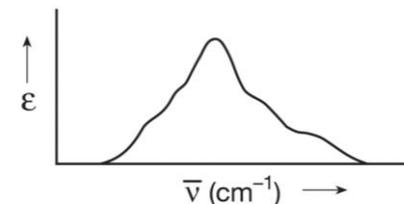
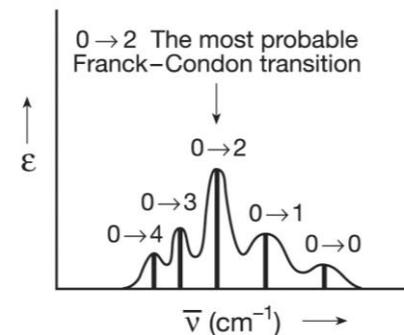
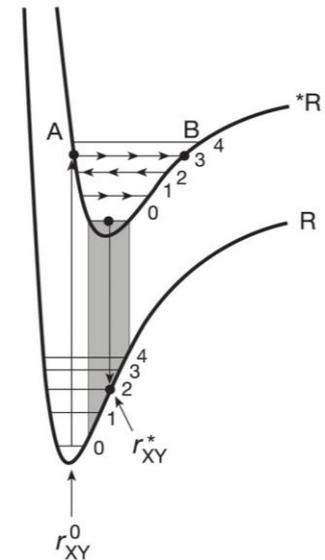
# Absorption Spectra of Organic Molecules

- In this example, of  $^*R$  to produce geometries more contracted than point C in the figure (points between B and C) results in dissociation of the diatomic molecule  $X-Y$  into two atoms,  $X + Y$
- When this happens, there is no vibrational structure in the absorption spectrum since the atoms dissociate immediately after absorbing a photon and do not undergo any vibrations



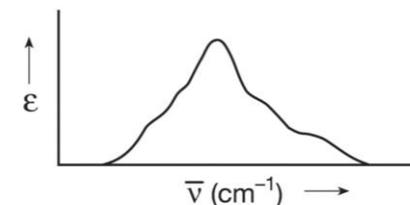
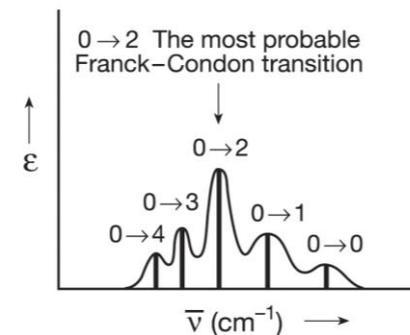
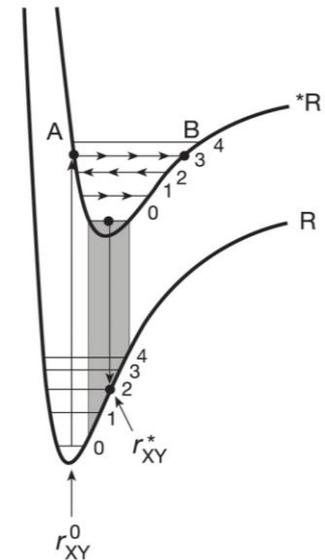
# The Franck-Condon Principle and Emission Spectra

- The rate of vibrational and electronic energy relaxation among excited states is very rapid compared to the rate of emission
- As a result, emission will generally occur only from the  $v = 0$  vibrational level of  $*R$
- Like absorption, the most probable emissions will be those that occur “vertically” with the smallest change in the value of the equilibrium geometry of  $*R$



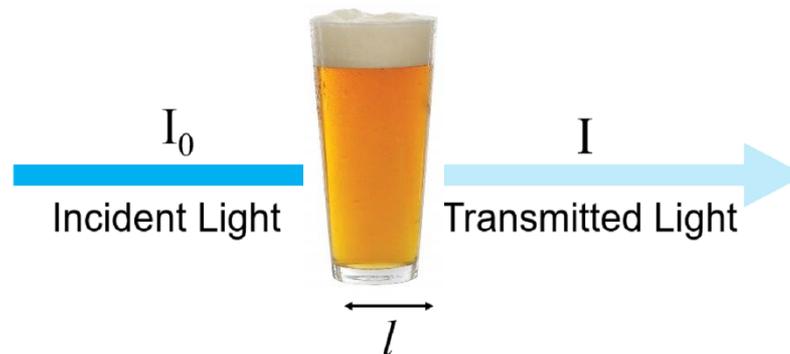
# The Franck-Condon Principle and Emission Spectra

- The frequency (energy) of the emission cannot be greater than the frequency (energy) of the  $0 \rightarrow 0$  emission, since the emissions from  $0 \rightarrow 1$ ,  $0 \rightarrow 2$ , etc. correspond to smaller energies than the  $0 \rightarrow 0$  emission
- Since the energy of the  $0 \rightarrow 0$  emission is the maximum energy that can be produced in the  $*R \rightarrow R + h\nu$  transition, this energy is defined as the excitation energy of the state and is given the symbol  $*E_S$  for the energy of  $*R(S_1)$  and the symbol  $*E_T$  for the energy of  $*R(T_1)$



# Absorption, Emission, and Excitation Spectra

- The experimental measurement of an *electronic absorption spectrum* is based off two important principles: Lambert's and Beer's law
- **Lambert's law** states that the proportion of light absorbed by a medium is independent of the initial intensity of the light,  $I_0$ 
  - Good for ordinary light sources, such as lamps, but breaks down when high-intensity lasers are employed
- **Beer's law** states that the amount of light absorbed is proportional to the concentration of absorbing molecules in the light path
  - Good approximation unless molecules begin to form aggregates at higher concentrations



# Absorption, Emission, and Excitation Spectra

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- The experimental quantity related to absorption that is typically measured is called **optical density (OD)**, eq 3), where  $I_0$  is the intensity of incident light falling on the sample and  $I_t$  is the intensity of light transmitted through the sample (usually understood to be 1 cm in depth)

$$OD = \log(I_0/I_t) \quad (3)$$

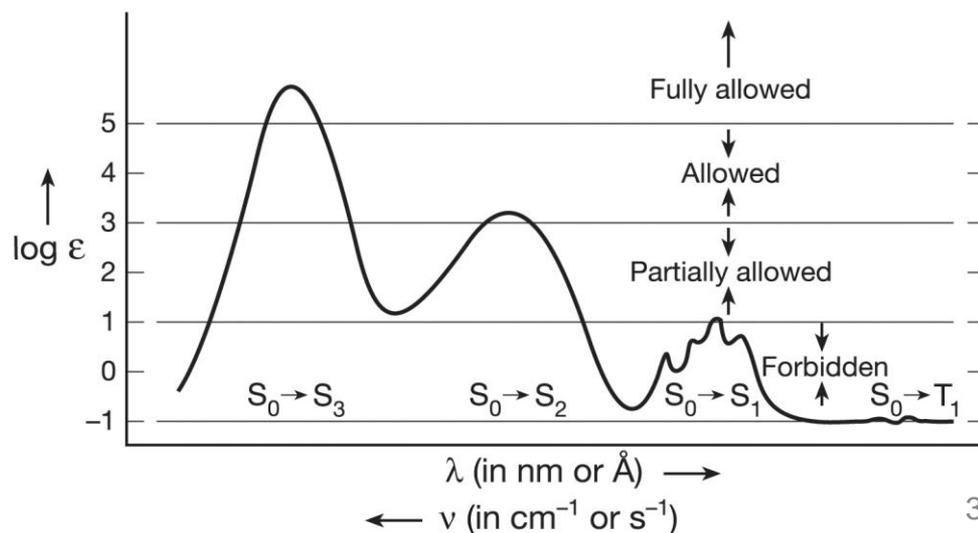
- For example,
  - OD = 2.0: ~1% transmission or ~99% absorption
  - OD = 1.0: ~10% transmission and 90% absorption
  - OD = 0.01: ~98% transmission and 2% absorption
- It is important to note that for a sample with an OD >2.0, most of the light is absorbed in a very small volume of the sample near to the place where light impinges on the sample

# Absorption, Emission, and Excitation Spectra

- An **absorption spectrum** is described by a graph of optical density versus the wavelength ( $\lambda$  units typically in nm, or Å)
- Conventionally, the **molar extinction coefficient** ( $\epsilon$ ) is employed in such graphs rather than absorption intensity, and is given by eq 4, where  $l$  is the optical path length (typically 1 cm), and  $[A]$  is the concentration of the absorbing material

$$\epsilon = [\log(I_0/I_t)]l[A] \quad (4)$$

- The coefficient ( $\epsilon$ ) is a fundamental molecular property and is independent of concentration and path length if Lambert's and Beer's laws hold
- Because of the wide variations of the values of  $\epsilon$ , absorption spectra are sometimes plotted as  $\log(\epsilon)$  vs.  $\lambda$
- Units of  $\epsilon$  are  $\text{cm}^{-1} \text{M}^{-1}$



# Absorption, Emission, and Excitation Spectra

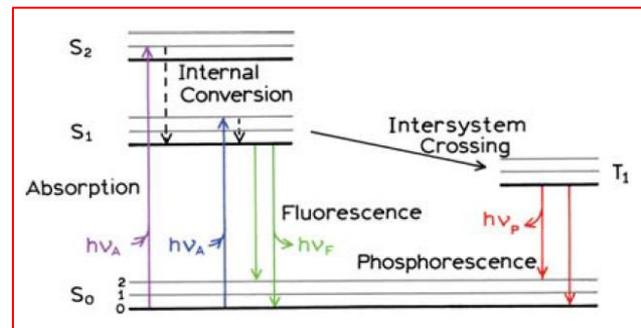
- An **emission spectrum** is a plot in nm of emission intensity  $I_e$  (at a fixed excitation wavelength and constant exciting intensity  $I_0$ ) as a function of wavelength of exiting light
- For a weakly absorbing species ( $OD < 0.1$ ) of a luminescent molecule A,  $I_e$  is given by eq 5:

$$I_e = 2.3 I_0 \varepsilon_A l \Phi^A [A] \quad (5)$$

- In eq 5,  $\varepsilon_A$  is the extinction coefficient of the absorbing molecule,  $l$  is the optical path length,  $\Phi^A$  is the quantum yield of emission of A (discussed later in the Chapter) and  $[A]$  is the concentration of A
- The quantum yield of emission,  $\Phi^A$ , is usually independent of the excitation wavelength (**Kasha's rule**)
- From eq 5, at fixed values of  $[A]$ ,  $I_0$ , and  $l$ , the intensity of the emitted light,  $I_e$ , is directly proportional to  $\varepsilon_A$
- A plot of  $I_e$  as a function of wavelength of exciting light that will vary as  $\varepsilon_A$  is termed an **excitation spectrum** and has the same spectral shape and appearance as an absorption spectrum

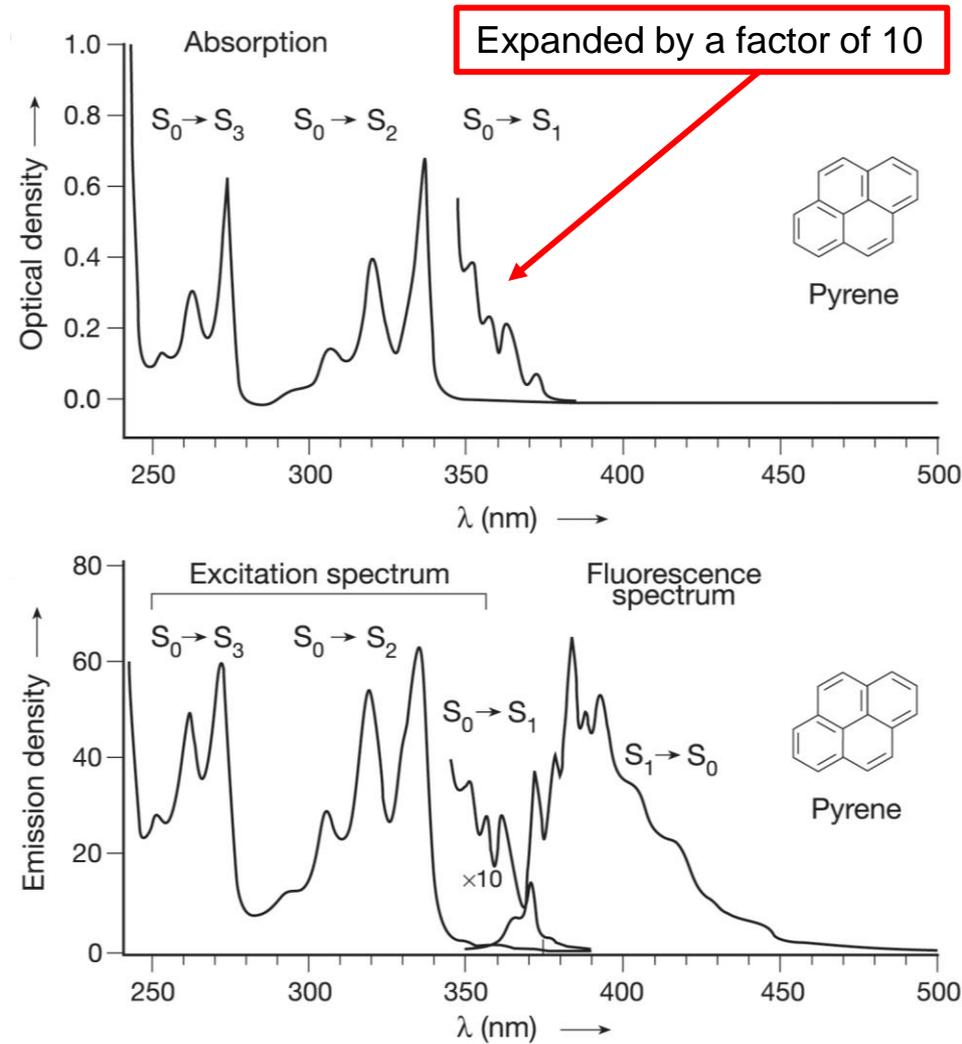
# The Stokes Shift

- Examination of a Jablonski diagram reveals that the energy of emission is typically less than that of absorption
  - Emission occurs at longer wavelengths
- First observed by Sir. George Gabriel Stokes in 1852 at the University of Cambridge
- One common cause of the **Stokes shift** is the rapid decay to the lowest vibrational level of  $S_1$
- Furthermore, lumophores generally decay to higher vibrational levels of  $S_0$ , resulting in further loss of excitation energy by thermalization of the excess vibrational energy



# Absorption, Emission, and Excitation Spectra

- Here is an example of an absorption, fluorescence, and fluorescence excitation spectrum of pyrene
- Notice the close resemblance of the absorption and excitation spectra
- Also note the relationship of the vibrational spectra of  $S_0 \rightarrow S_1$  absorption and the  $S_1 \rightarrow S_0$  fluorescence
- Absorption spectrum is “mirror image” of fluorescence spectrum (**mirror image rule**)
- Note that the emission spectrum is the mirror image of the  $S_0 \rightarrow S_1$  absorption, not the entire absorption spectrum



# Order of Magnitude Estimates of Radiative Transition Parameters

---

- **Reminder:** Spin-allowed refers to transitions that do not involve a change in spin multiplicity
- The probability ( $\epsilon$ ) of spin-allowed radiative transitions can range over four orders of magnitude
- Therefore, there is a range of “allowedness” in radiative transitions
- *We must understand that the terms “allowed” and “forbidden” are relative and not absolute*
- We need to think of these terms as the *relative* probability, or rate of one type of process compared to another

# Order of Magnitude Estimates of Radiative Transition Parameters

- The table below has some representative values (order of magnitude only) of  $\epsilon_{\max}$  and the rate of emission ( $k_e^0$ ) for transitions of various molecules

	$k_e^0$ ( $s^{-1}$ )	Example	Transition Type	$\epsilon_{\max}$	$\nu_{\max}$ ( $cm^{-1}$ )
Spin Allowed	$10^9$	<i>p</i> -Terphenyl	$S_1(\pi, \pi^*) \leftrightarrow S_0$	$3 \times 10^4$	30,000
	$10^8$	Perylene	$S_1(\pi, \pi^*) \leftrightarrow S_0$	$4 \times 10^4$	22,850
	$10^7$	1,4-Dimethylbenzene	$S_1(\pi, \pi^*) \leftrightarrow S_0$	$7 \times 10^2$	36,000
	$10^6$	Pyrene	$S_1(\pi, \pi^*) \leftrightarrow S_0$	$5 \times 10^2$	26,850
	$10^5$	Acetone	$S_1(n, \pi^*) \leftrightarrow S_0$	10	~30,000
Spin Forbidden	$10^4$	Xanthone	$T_1(n, \pi^*) \leftrightarrow S_0$	1	~15,000
	$10^3$	Acetone	$T_1(n, \pi^*) \leftrightarrow S_0$	$10^{-1}$	~27,000
	$10^2$	1-Bromonaphthalene	$T_1(\pi, \pi^*) \leftrightarrow S_0$	$10^{-2}$	20,000
	10	1-Chloronaphthalene	$T_1(\pi, \pi^*) \leftrightarrow S_0$	$10^{-3}$	20,600
	$10^{-1}$	Naphthalene	$T_1(\pi, \pi^*) \leftrightarrow S_0$	$10^{-4}$	~21,300

# Order of Magnitude Estimates of Radiative Transition Parameters

---

## Important aspects to take note from the previous table:

- The larger the value for  $\varepsilon_{\max}$ , the more probable (more allowed) the transition
- The more probable the absorption (the larger the value of  $\varepsilon_{\max}$ ), the faster the related emission ( $k_e^0$ )
- Rate of emission also depends on the wavelength of emission, which determines the frequency of emission

# Order of Magnitude Estimates of Radiative Transition Parameters

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- An important conclusion from these data is that even for spin-allowed transitions, there are factors that cause a certain degree of “forbiddenness” to absorption and emission
- Let’s examine the different “forbiddenness factors”:
  - **Orbital forbiddenness**, which results from poor spatial overlap of the orbitals involved in the HO  $\rightarrow$  LU transition
    - Example is the  $n, \pi^*$  transition of ketones, for which the HO and LU are orthogonal to one another and the overlap is close to zero
  - **Orbital symmetry forbiddenness**, which results from orbital wave functions (involved in the transition) that overlap in space but have their overlap integral canceled because of symmetry of the wave functions
    - Examples are the  $S_0 + h\nu \rightarrow S_1(\pi, \pi^*)$  and  $S_1(\pi, \pi^*) \rightarrow S_0 + h\nu$  transitions in benzene, naphthalene, and pyrene
    - Further details on this is outside of the scope of the textbook and this course

# Order of Magnitude Estimates of Radiative Transition Parameters

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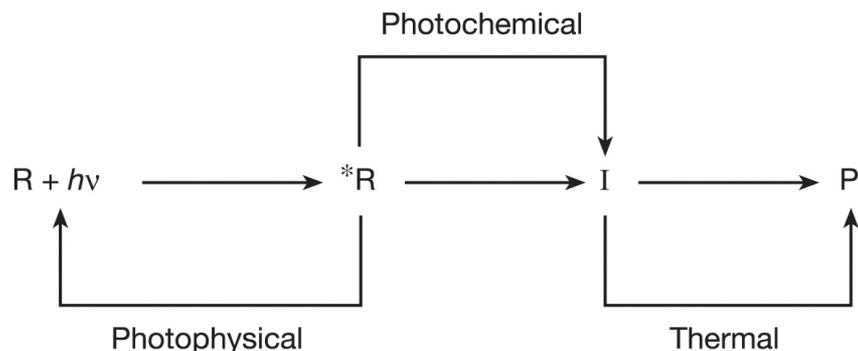
- To the photochemist, an idea of limiting values of the **fluorescence rate constant** ( $k_F^0$ ) is important to calibrate the maximum time allowed for reaction in  $S_1$ 
  - If reaction from  $S_1$  is to occur efficiently, it must be competitive with  $k_F^0$
- From the prior table, we can see that a benchmark for the largest  $k_F^0$  is  $\sim 10^9 \text{ s}^{-1}$  for *p*-terphenyl (a fully allowed  $\pi \rightarrow \pi^*$  transition) and the smallest  $k_F^0$  is  $\sim 10^5 \text{ s}^{-1}$  for acetone (a weakly allowed  $n \rightarrow \pi^*$  transition)
- This provides two useful calibration rules
  - If  $^*R$  possesses a lifetime shorter than  $10^{-9} \text{ s}$ , its lifetime is limited not by fluorescence but by some photophysical or radiationless process
  - If  $^*R$  possesses a lifetime longer than  $10^{-5} \text{ s}$ , it cannot be a singlet state

# Order of Magnitude Estimates of Radiative Transition Parameters

---

- As a benchmark for spin-forbidden transitions, the largest value of the **phosphorescence rate constant** ( $k_p^0$ ) is on the order of  $10^3 \text{ s}^{-1}$  (lifetime  $10^{-3} \text{ s}$ ), and the smallest value of  $k_p^0$  is on the order of  $10^{-1} \text{ s}^{-1}$  (lifetime  $10 \text{ s}$ )
- Thus,  $^*R(T_1)$  will persist many orders of magnitude longer than  $^*R(S_1)$  before emitting a photon
- This long-lifetime characteristic of triplets has important implications concerning their photochemistry

# Quantum Yields for Emission



Scheme 2.1 copyright 2009 University Science Books

- The rate constants of photophysical and photochemical processes from  $*R(S_1)$  and  $*R(T_1)$  determine the efficiencies of the processes that occur from these electronically excited states
- The **quantum yield** ( $\Phi$ ) is an efficiency parameter measuring the fraction of absorbed photons that produces a specific sequence shown in the paradigm of organic photochemistry (see Scheme above)
- The parameter  $\Phi$  may be expressed in molar terms (the number of moles of  $*R$  that proceed along a pathway in the Scheme relative to the number of moles of photons absorbed by  $R$ ) or in kinetic terms (the rate of the pathway of interest from  $*R$  compared to the sum of all the rates of all pathways for decay of  $*R$ )

# Quantum Yields for Emission

- **Reminder:** **Kasha's rule** states that upon photoexcitation of an organic molecule, only fluorescence from a thermally equilibrated  $S_1$  state or phosphorescence from a thermally equilibrated  $T_1$  state is observed experimentally
- Whether any emission is observed at all from  $S_1$  or  $T_1$  for an organic molecule is determined by the experimental quantum yield for emission ( $\Phi_F$  for fluorescence and  $\Phi_P$  for phosphorescence)
- The value of  $\Phi$  is a direct and absolute measure of the efficiency of an emission process and is defined as photons out (emitted) vs. photons in (absorbed)

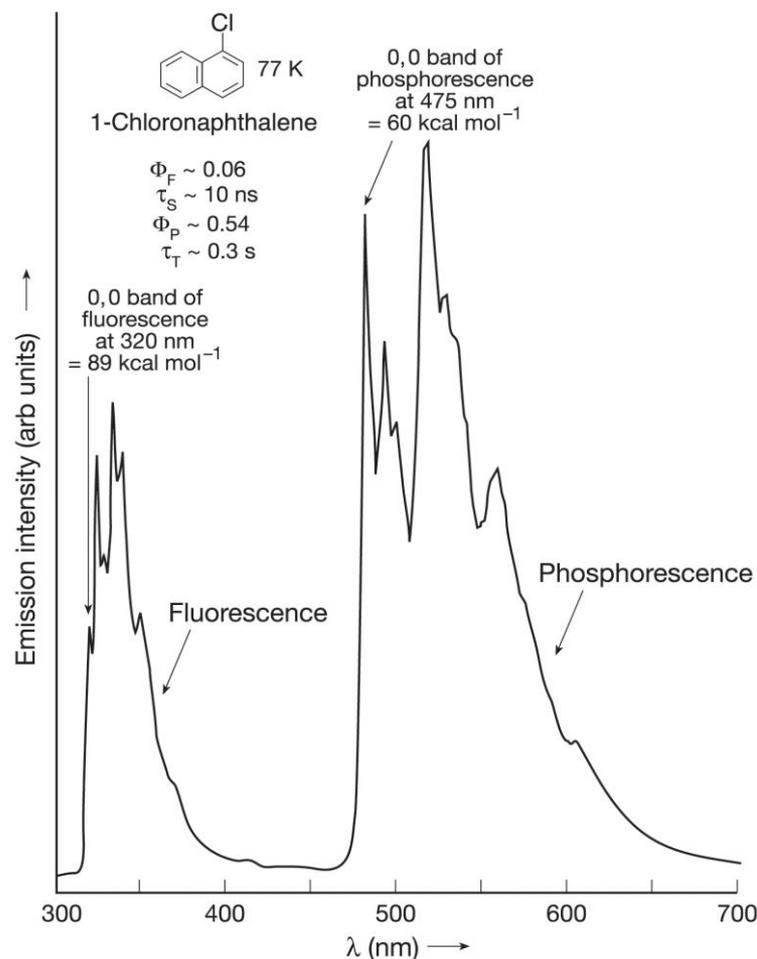


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## Quantum Yields for Emission

- A general expression for the **quantum yield of emission** ( $\Phi_e$ ) from a specific state,  ${}^*R(S_1)$  or  ${}^*R(T_1)$ , is given by eq 6:

$$\Phi_e = {}^*\Phi k_e^0 (k_e^0 + \sum k_i)^{-1} = {}^*\Phi k_e^0 \tau \quad (6)$$

where  ${}^*\Phi$  is the formation efficiency of the given state,  $k_e^0$  is the rate constant for emission of the given state ( $k_F^0$  or  $k_P^0$ ), and  $\sum k_i$  is the sum of all rate constants that radiationlessly deactivate the emitting state, that is:

$$\tau = (k_e^0 + \sum k_i)^{-1}$$

- The **experimental lifetime** ( $\tau$ ), and therefore the experimental quantum yield of emission,  $\Phi_e$ , depend crucially on the magnitude of  $\sum k_i$  relative to  $k_e^0$

# Quantum Yields for Emission

---

- In order to observe electronic emission spectra routinely, *it is usually necessary to minimize  $\sum k_i$*
- This is accomplished by cooling the sample to 77 K (the boiling point of liquid N<sub>2</sub>) and/or by making the sample a rigid solid, such as a polymer (all organic solvents are solids at 77 K)
- Numerous solvents form optically clear solid solutions at 77 K and are called **glasses** at this temperature
- Low temperature causes terms in  $\sum k_i$  to become small relative to  $k_e$ , such as restricting molecular motion (twisting of C=C bonds or stretching of C–C bonds), which are effective at promoting physical and chemical radiationless transitions
- Sample rigidity also eliminates terms in  $\sum k_i$  that are due to bimolecular quenching processes, since diffusion has been eliminated

## Quantum Yields for Emission

---

- Even when emission spectra are measured at 77 K, the total quantum yields of emission ( $\Phi_F + \Phi_P$ ) are generally  $< 1.00$
- Some radiationless processes still occur even at 77 K, as shown in eq 7:

$$\Phi_F + \Phi_P + \sum \Phi_R = 1 \quad (7)$$

- In eq 7,  $\sum \Phi_R$  is the sum of quantum yields for photochemical and photophysical radiationless transitions from  $S_1$  and  $T_1$

# Quantum Yields for Emission

- Data derived from fluorescence spectra at 77 K are conveniently analyzed and interpreted in terms of eq 8, which is a specific form of eq 6 [ $k_e^0 = k_F^0$ ;  $\sum k_i = k_{ST}$  (rate of ISC)]:

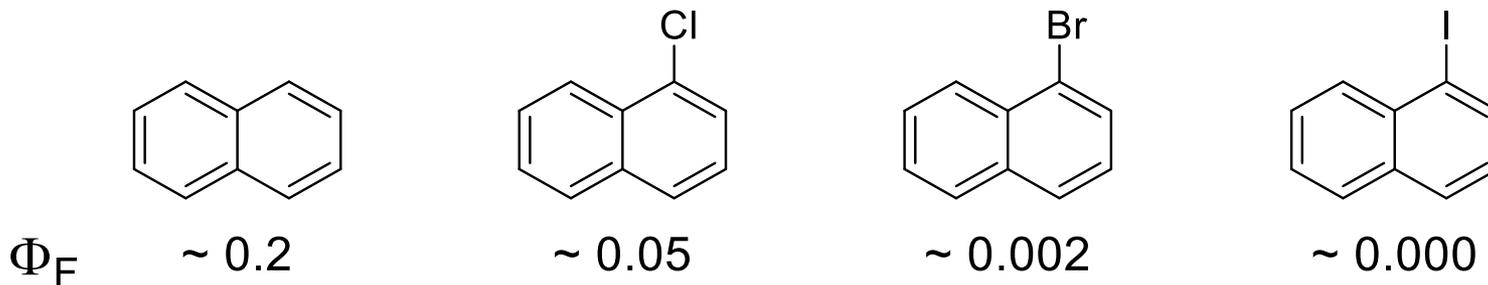
$$\Phi_F = k_F^0(k_F^0 + k_{ST})^{-1} = k_F^0\tau_S \quad (8)$$

where  $\tau_S$  is defined as  $(k_F^0 + k_{ST})^{-1}$

- Eq 8 has two limiting situations:
  - 1)  $k_F^0 \gg k_{ST}$ , in which case  $\Phi_F \sim 1.00$
  - 2)  $k_F^0 \ll k_{ST}$ , in which case  $\Phi_F = k_F^0/k_{ST}$
- Thus, it is expected that simply upon consideration of the competition between fluorescence and intersystem crossing from  $S_1$ , the value of  $\Phi_F$  can vary over orders of magnitude

## Experimental Examples of $\Phi_F$

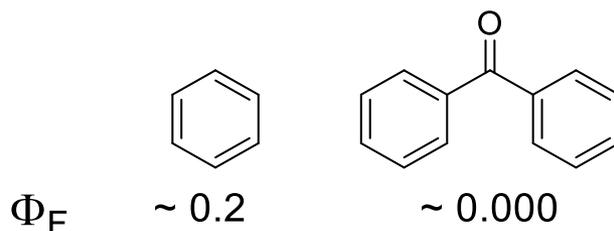
- When examining available literature data for  $\Phi_F$  at 77 K, some generalizations can be made:
  - Most rigid aromatic hydrocarbons (benzene, naphthalene, anthracene, etc.) and their derivatives possess measurable, but variable, fluorescence quantum yields ( $1 > \Phi_F > 0.01$ ), even at 77 K
  - Low values of  $\Phi_F$  for non rigid aromatic hydrocarbons are common and usually the result of competing internal conversion ( $S_1 \rightarrow S_0$ ) or intersystem crossing ( $S_1 \rightarrow T_1$ ) triggered by molecular motion
  - Substitution of Cl, Br, or I for H on an aromatic ring generally results in a decrease in  $\Phi_F$  such that  $\Phi_F^H > \Phi_F^F > \Phi_F^{Cl} > \Phi_F^{Br} > \Phi_F^I$



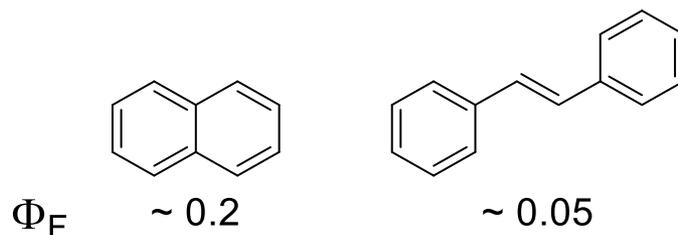
## Experimental Examples of $\Phi_F$

- When examining available literature data for  $\Phi_F$  at 77 K, some generalizations can be made:

- Substitution of C=O for H on an aromatic ring generally results in a substantial decrease in  $\Phi_F$



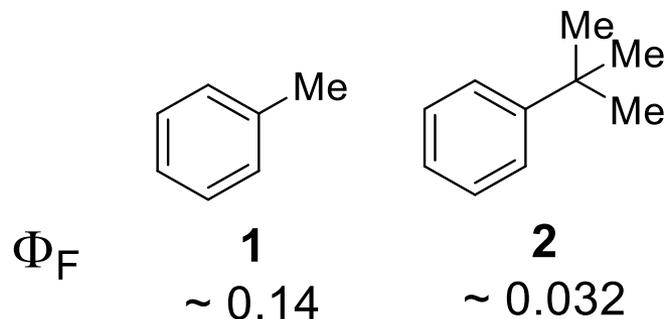
- Molecular rigidity (due to structural or environmental constraints) enhances  $\Phi_F$



- For rigid aromatics, internal conversion does not compete favorably with fluorescence or intersystem crossing

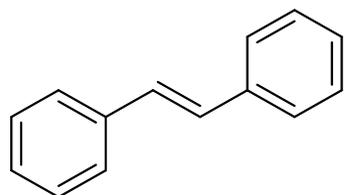
## Experimental Examples of $\Phi_F$

- Saturated compounds and simple alkenes, such as ethylenes and polyenes, do not fluoresce efficiently
- Short lifetimes and low emission efficiencies are typical of “flexible” molecules for which a rapid radiationless deactivation may occur via a stretching motion along the C–C (or C–H) bond or via a twisting motion about a C=C bond
- As an example of the role of stretching motions in determining  $\Phi_F$ , let's compare the aromatic hydrocarbons toluene (**1**) and *tert*-butyl benzene (**2**)

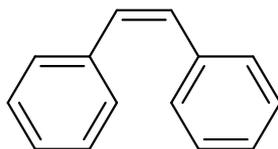


# Experimental Examples of $\Phi_F$

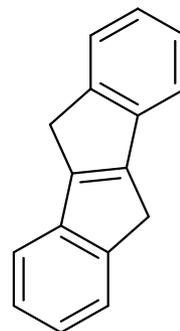
- For the role of twisting motion in determining  $\Phi_F$ , let's consider *trans*- and *cis*-stilbene (**3** and **4**, respectively) and their rigid cyclic derivatives **5** and **6**



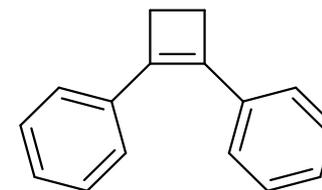
**3**  
*trans*-stilbene



**4**  
*cis*-stilbene



**5**



**6**

Temperature	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>
25 °C	0.05	0.00	~ 1.0	~ 1.0
77 K	0.75	0.75	~ 1.0	~ 1.0

# Determination of $E_S$ and $E_T$ from Emission Spectra

---

- The electronic energy of  $^*R$  is an important property since it can be used as free energy to drive photochemical reactions
- For example, the higher the energy of  $^*R$ , the stronger the bonds that can be broken in a primary photochemical process
- The electronic energy  $^*R$  may be determined directly from its emission spectrum
- The highest energy (highest frequency, shortest wavelength) vibrational band in an emission spectrum corresponds to the 0,0 transition
- The energy gap corresponding to the 0,0 transition characterizes the energy of  $^*R$  which is responsible for the emission

# Determination of $E_S$ and $E_T$ from Emission Spectra

- The singlet-state energy ( $E_S$ ) and the triplet state energy ( $E_T$ ) are defined as the 0,0 energy gap for fluorescence,  $S_1(\nu = 0) \rightarrow S_0(\nu = 0)$ , and phosphorescence,  $T_1(\nu = 0) \rightarrow S_0(\nu = 0)$ , respectively

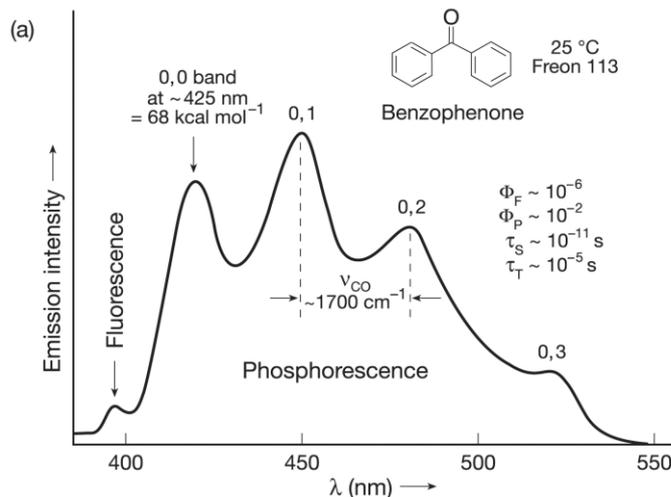
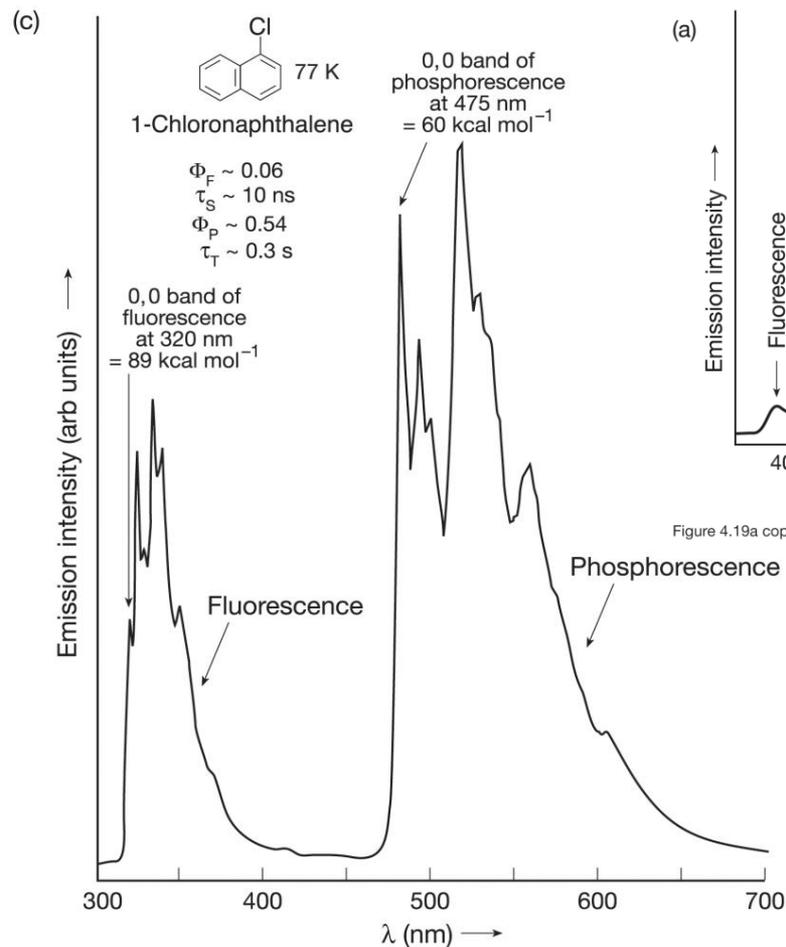


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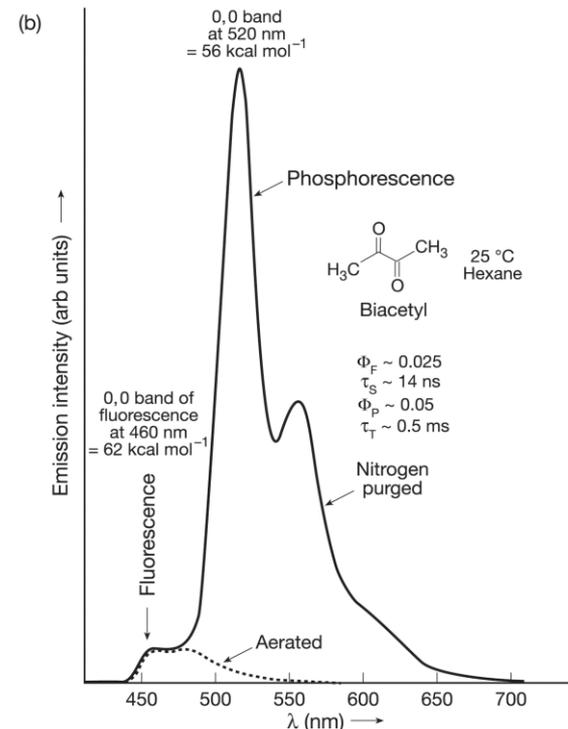


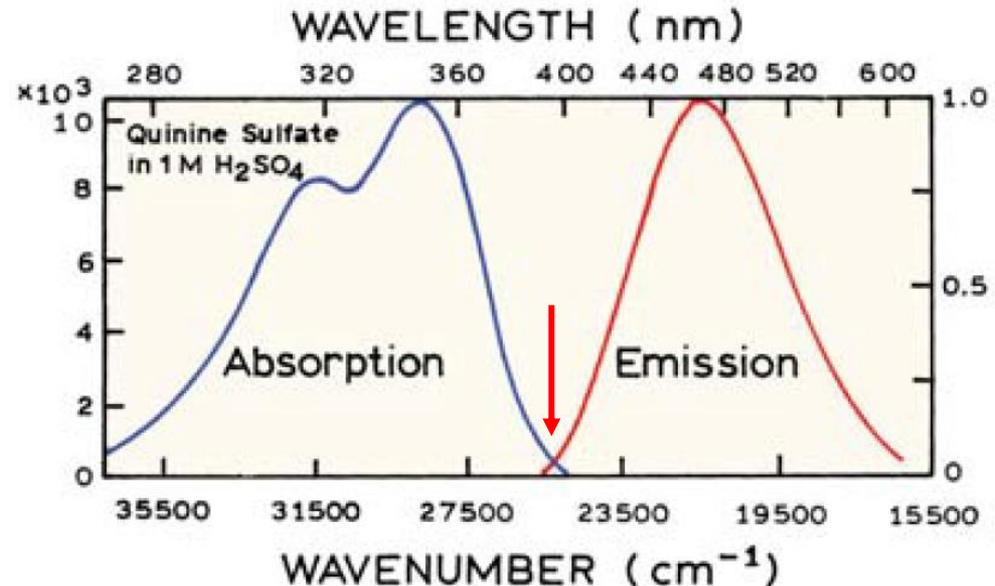
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# Determination of $E_S$ and $E_T$ from Emission Spectra

**Question:** What if the emission spectrum does not show sufficiently resolved fine structure for an accurate estimate of  $E_S$  or  $E_T$  to be made?

- In other words, what if the emission spectrum is a featureless band?
- In this case, you would use the “onset” or the high-energy (short-wavelength) portion of the emission

**Note:** If the absorption and emission bands intersect, like in this example, the intersection wavelength can be used to estimate  $E_{0,0}$



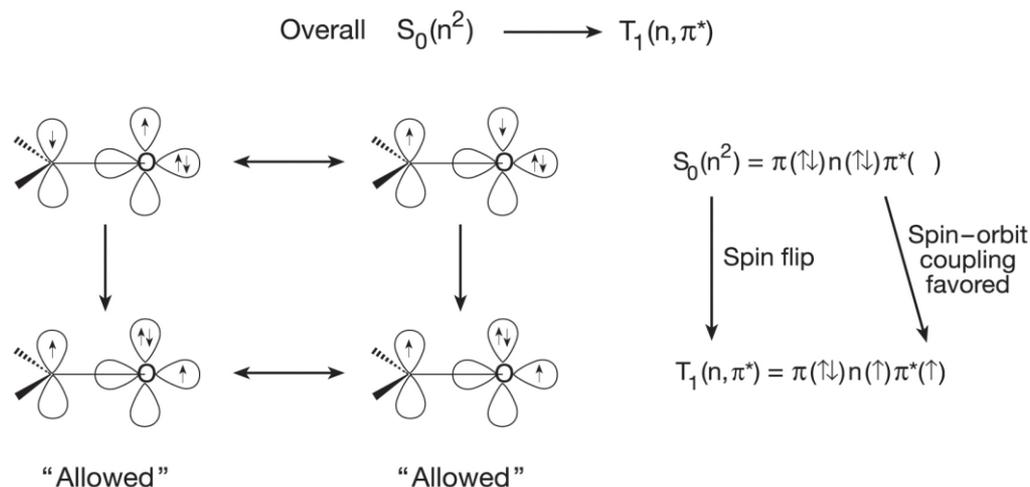
# Spin–Orbit Coupling and Spin Forbidden Radiative Transitions

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- The radiative  $S_0 \rightarrow T_1$  and  $T_1 \rightarrow S_0$  processes are formally “spin-forbidden” but nonetheless are generally observed experimentally
- The magnitude of the values of  $\varepsilon(S_0 \rightarrow T_1)$  or of  $k_p^0(T_1 \rightarrow S_0)$  is directly related to the degree of **spin–orbit coupling** that mixes  $S_0$  and T
- From Chapter 3, the degree of spin–orbit coupling was shown to depend strongly on:
  - a) The ability of the electrons in the HO or LU of \*R to approach a nucleus closely
  - b) The magnitude of positive charge (atomic number) of the nucleus that the HO or LU electrons approach and experience
  - c) The availability of transitions between orthogonal orbitals
  - d) The availability of a “one-atom center”  $p_x \rightarrow p_y$  transition that can generate orbital angular momentum that could couple with spin angular momentum

# Radiative Transitions Involving a Change in Multiplicity

- Let's consider the radiative  $S_0(n^2) + h\nu \rightarrow T_1(n, \pi^*)$  transition for formaldehyde
- The spin change for formaldehyde is due to a  $n \rightarrow \pi^*$  transition, which may be viewed as a jump from a p orbital localized on oxygen (say  $p_x$ ) in the plane of the molecule to a p orbital (say  $p_y$ ) perpendicular to the plane of the molecule
- The simultaneous  $p_x \rightarrow p_y$  orbital jump is this a one-center jump involving orbital angular momentum change
- *This type of situation is precisely what is required for generating angular momentum and favors strong spin-orbit coupling*



# Radiative Transitions Involving a Change in Multiplicity

- Let us compare this to the situation for a radiative  $S(\pi^2) \rightarrow T(\pi, \pi^*)$  transition for ethylene
- As you can see from looking at its planar ground state, the analogue of the low energy  $p_x \rightarrow p_y$  jump of ketones does not exist for ethylene
- Consequently, there are no “one-center” spin-orbit interactions that help flip the spins when a light wave interacts with the  $\pi$  electrons of ethylene and spin-orbit coupling is inhibited
- *We can conclude the magnitude of spin-orbit coupling is much larger for  $n^2 \rightarrow n, \pi^*$  transitions than for  $\pi^2 \rightarrow \pi, \pi^*$  transitions. This is a general situation for organic molecules and known as **El-Sayed's rule***

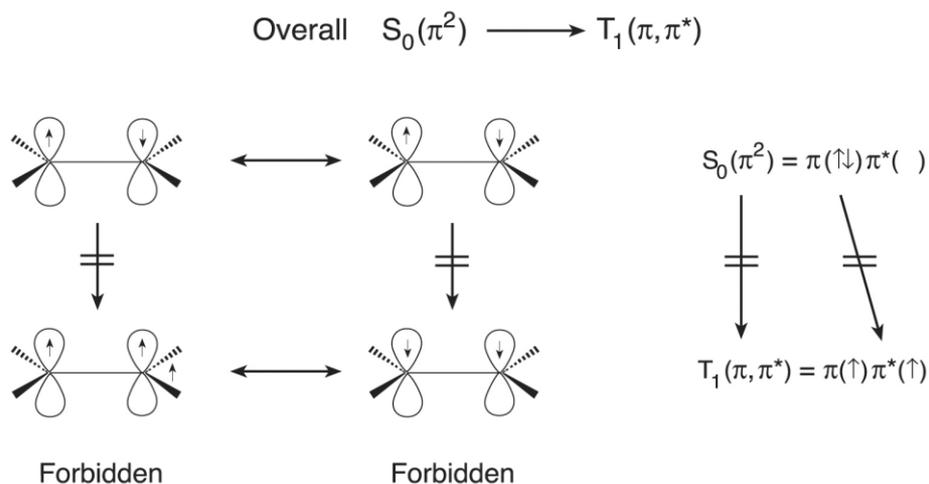


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# Experimental Exemplars of Spin-Forbidden Radiative Transitions

- Some experimental data for radiative  $S_0 \rightarrow T_1$  transitions are given in the Table below
- From the table, we can see that the largest values for  $k_p^0$  are found for  $T_1(n,\pi^*)$  states or for  $T_1(\pi,\pi^*)$  states that possess a heavy atom conjugated to the  $\pi$  system

Compound	$\Phi_P$ (77 K)	$\Phi_{ST}$	$k_p^0$ (s <sup>-1</sup> )	Configuration of $T_1$
Benzene	~0.2	~0.7	~10 <sup>-1</sup>	$\pi,\pi^*$
Naphthalene	~0.05	~0.7	~10 <sup>-1</sup>	$\pi,\pi^*$
1-Fluoronaphthalene	~0.05		~0.3	$\pi,\pi^*$
1-Chloronaphthalene	~0.3	~1.0	~2	$\pi,\pi^*$
1-Bromonaphthalene	~0.3	~1.0	~30	$\pi,\pi^*$
1-Iodonaphthalene	~0.4	~1.0	~300	$\pi,\pi^*$
Triphenylene	~0.5	~0.9	~10 <sup>-1</sup>	$\pi,\pi^*$
Benzophenone	~0.9	~1.0	~10 <sup>2</sup>	$n,\pi^*$
Biacetyl	~0.3	~1.0	~10 <sup>2</sup>	$n,\pi^*$
Acetone	~0.3	~1.0	~10 <sup>2</sup>	$n,\pi^*$
Acetophenone	~0.7	~1.0	~10 <sup>2</sup>	$n,\pi^*$

## The $T_1 \rightarrow S_0 + h\nu$ Process

---

- A general expression for the quantum yield of phosphorescence ( $\Phi_P$ ) is given by eq 9:

$$\Phi_P = \Phi_{ST} k_P^0 (k_P^0 + \sum k_d + \sum k_q [Q])^{-1} = \Phi_{ST} k_P^0 \tau_T \quad (9)$$

- In eq 9,  $\Phi_{ST}$  is the quantum yield of intersystem crossing,  $S_1 \rightarrow T_1$ ;  $k_P^0$  is the radiative rate of phosphorescence;  $\sum k_d$  is the sum of all unimolecular radiationless deactivations of  $T_1$  (including photochemical reactions); and  $\sum k_q [Q]$  is the sum of all biomolecular deactivations of  $T_1$  (including photochemical reactions)
- From eq 9, we can see that  $\Phi_P$  is the product of multiple factors
- Unless these factors can be experimentally identified and controlled,  $\Phi_P$  is not a reliable parameter to characterize  $T_1$

## The $T_1 \rightarrow S_0 + h\nu$ Process

---

- The Table in the prior slide has the data for the  $\Phi_p$  for a variety of molecules at 77 K in rigid glasses
- At 77 K, all bimolecular diffusional deactivation processes ( $\sum k_q[Q]$  term) are inhibited (diffusion has been eliminated), so that the main radiationless deactivation of  $T_1$  is the  $T_1 \rightarrow S_0$  intersystem crossing
- In this limited case,  $\Phi_p$  can be simplified to eq 10; that is, the value of  $\Phi_p$  depends only on the value of  $\Phi_{ST}$  and the competition between rates of phosphorescence emission ( $k_p^0$ ) and intersystem crossing ( $k_{TS}$ )

$$\Phi_p = \Phi_{ST} k_p^0 (k_p^0 + k_{TS})^{-1} \quad (\text{at } 77 \text{ K}) \quad (10)$$

# Absorption Complexes and Exciplexes

---

- To this point, we've only considered absorption and emission processes of a single molecule
- In certain cases, two or more molecules may participate in cooperative absorption or emission; that is, the absorption or emission can only be understood as arising from ground- or excited-state complexes
- Commonly, the stoichiometry of such complexes consists of two molecules
- When two molecules act cooperatively to absorb a photon, we say that an *absorption complex* exists in the ground state and is responsible for absorption
- If two molecules act cooperatively to emit a photon to a dissociative ground state, we say an *exciplex* exists

# Absorption Complexes and Exciplexes

---

- Some significant experimental spectroscopic characteristics include:
  1. **Absorption complex**: The observation of a new absorption band, typically at longer wavelengths than the absorption of either molecular component, that is characteristic of the complex but not of either of the individual molecular components
  2. **Exciplex**: The observation of a new emission band, usually structureless and at longer wavelengths than the absorption for either of the molecular components, that is characteristic of the exciplex and not of the individual components
  3. **Absorption Complex and Exciplex**: A concentration dependence of the new absorption or emission intensity

# Absorption Complexes and Exciplexes

---

- In the special case, where the molecular components of the exciplex are the same, the excited molecular complex is termed an “**excimer**”
  - **Excited-state Dimer**
- **Exciplex** is reserved for excited-state complexes consisting of two different molecular components
  - **Excited-state Complex**

# Ground-State Charge-Transfer Absorption Complexes

- Solutions of mixtures of molecules that possess low ionization (electron donors, D) or a high electron affinity (electron acceptors, A) often exhibit absorption bands that are not shown separately by either component
- Generally, the new band is due to an **electron donor-acceptor (EDA)** or **charge-transfer (CT) complex** in which D has donated an electron (charge) to a certain extent to A

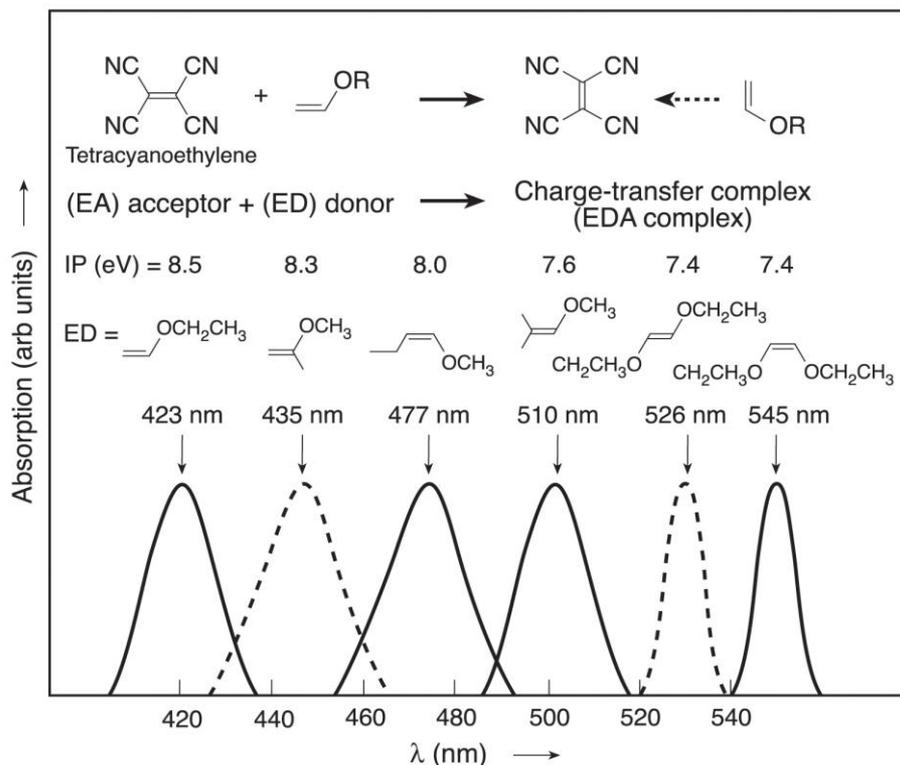


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# Ground-State Charge-Transfer Absorption Complexes

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- Generally, *the absorption band of an EDA complex is broad and devoid of vibrational structure*
- This breadth occurs because the rather small binding energies of EDA complexes allows many different structural configurations for the complex to exist in equilibrium with one another
- The absorption energy of each configuration will differ and cause a broadening of the band
- Since the bonding is weak and intermolecular, there are no characteristic vibrational bands that appear in the spectra

# Excimers and Exciplexes

---

- Consider a pair of molecules **R** and **N** for which **R** absorbs a photon to form **\*R** and then **\*R** collides with **N**
- What factors contribute to the stability of an excited-state complex, **R-<sup>\*</sup>-N** (where excitation is shared to some extent by both molecular components) that are missing in the ground state complex, **R/N**?
- An electronically excited-state **\*R** possesses a much stronger electron affinity and a much lower ionization potential than the ground state, because of the occurrence of an electrophilic half-filled HO and a nucleophilic half-filled LU
  - More on this in Chapter 7
- Consequently, these orbitals may participate in CT interactions with other polar or polarizable species they encounter intermolecularly

# Excimers and Exciplexes

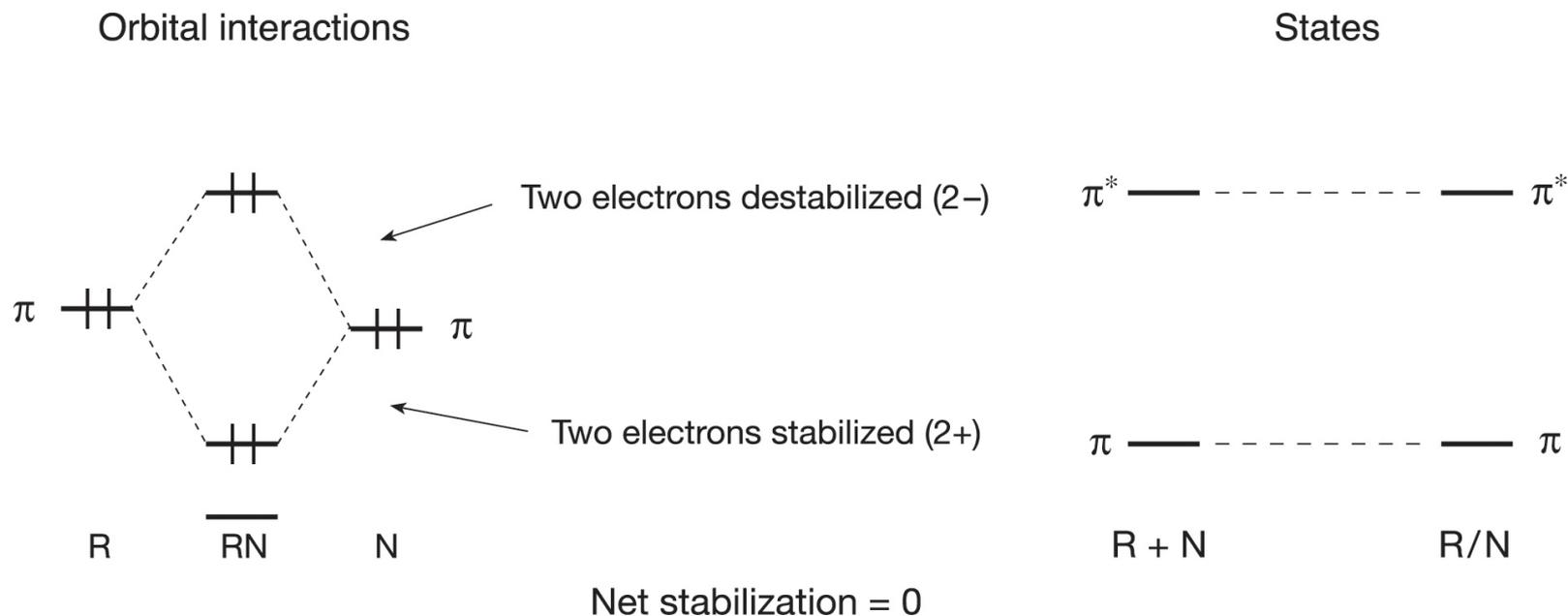
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- A collision between  $^*R$  with any polar or polarizable ground-state molecule,  $N$ , will generally be stabilized by some CT interaction involving the HO or LU of  $^*R$  with  $N$
- This energetic stabilization will in turn cause the  $R\text{-}^*\text{-}N$  collision complex to possess a longer lifetime than the corresponding ground-state collision complex
- The  $R\text{-}^*\text{-}N$  collision complex should possess observable spectroscopic and chemical properties that are distinct from those of  $^*R$
- When this is the case,  $R\text{-}^*\text{-}N$  is considered a supramolecular electronically excited species, held together by attractive intermolecular forces



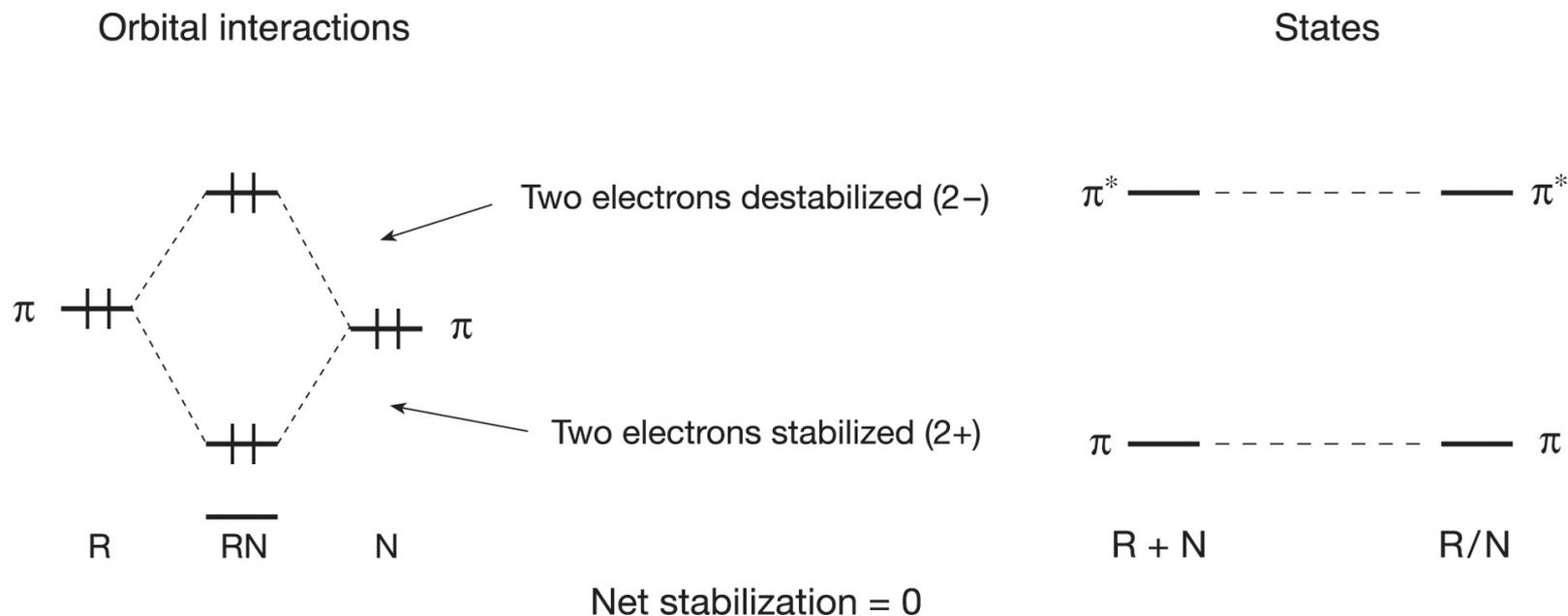
# Excimers and Exciplexes

- A theoretical basis for the enhanced stabilization of a  $R^*-N$  collision pair relative to a  $R/N$  ground-state collision complex is available from the simple theory of MO interactions
- In the collision complex of the ground-state molecules  $R$  and  $N$ , the four electrons that occupied the HOs of  $R$  and  $N$  occupy the new set of MOs according the Aufbau principle and fill the lowest-energy orbital
- Two electrons are stabilized in the HO and two are destabilized in the LU



# Excimers and Exciplexes

No gain in energy is achieved by interacting  $R$  and  $N$  during their ground-state collisions since the bonding and antibonding interactions cancel each other out



# Excimers and Exciplexes

- *In the exciplex*, since one of the partners ( $*R$ ) is electronically excited, three electrons are stabilized (two in lower-energy HO and one in lower-energy LU)
- Only one electron is destabilized (in the higher energy HO) as the electrons redistribute themselves from their original non-interacting orbitals to the new orbitals of the exciplex

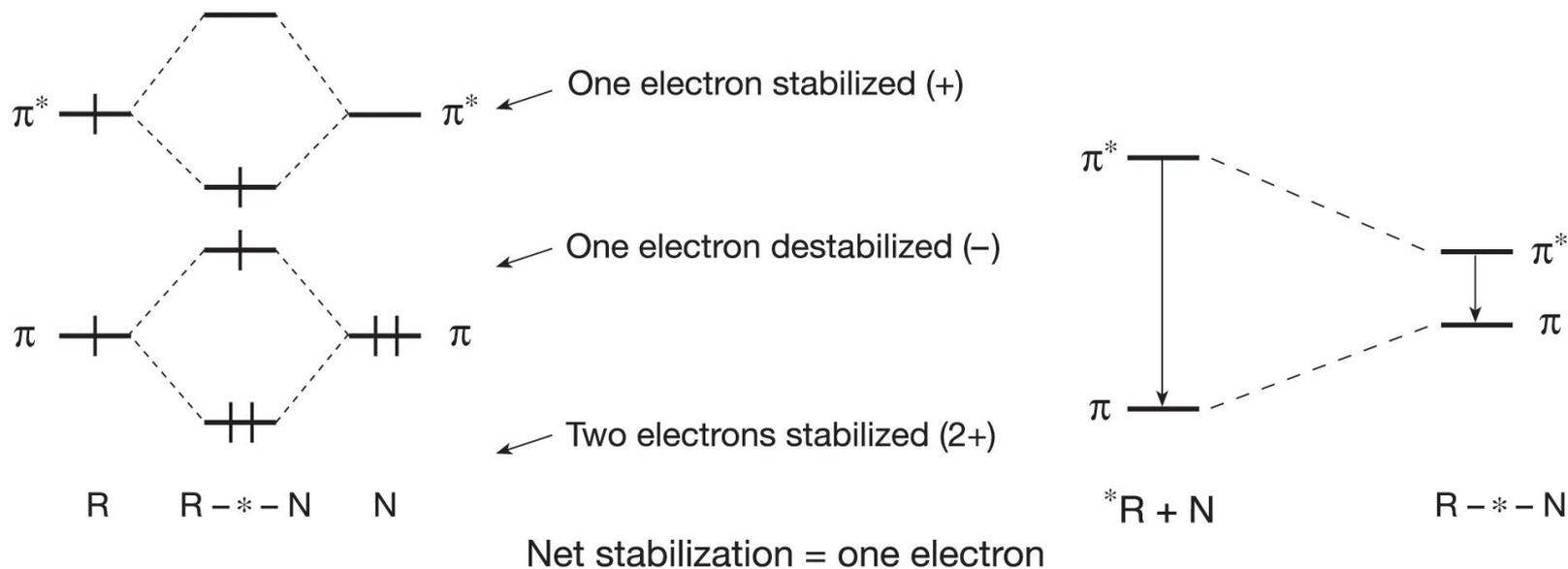


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# Excimers and Exciplexes

*A net gain in energy is always achieved by interaction of  $^*R$  and  $N$  during their collisions!*

- We can conclude from this analysis that  $^*R$  has an inherent tendency to form a supramolecular complex with other molecules

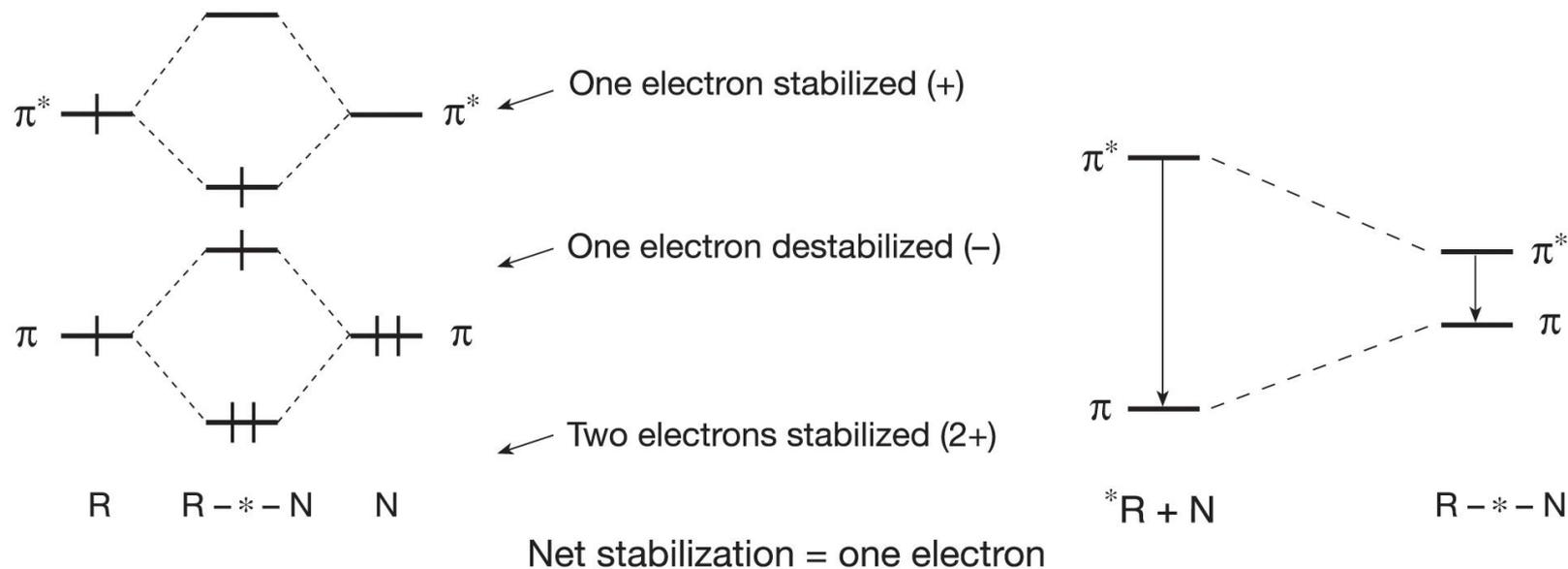


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# Excimers and Exciplexes

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Question: Based on the prior analysis, shouldn't all molecules associate in the excited state?

No, it depends on the strength of the excimer or exciplex binding

- If there is only a very weak interaction between  $^*R$  and  $N$ , the emission of the collision complex will look very much like that of the monomer  $^*R$ , and the energy of the emission will be close to that for the  $^*R \rightarrow R + h\nu$  process
- If the orbital interactions between  $^*R$  and  $N$  are sufficiently strong, the collision complex between  $^*R$  and  $N$  becomes an exciplex ( $R-^*-N$ ), and the energy of the latter decreases relative to that of the ground-state complex ( $R/N$ )
- The emission ( $R-^*-N$ )  $\rightarrow R/N + h\nu$  produces the unstable, ground-state collision complex

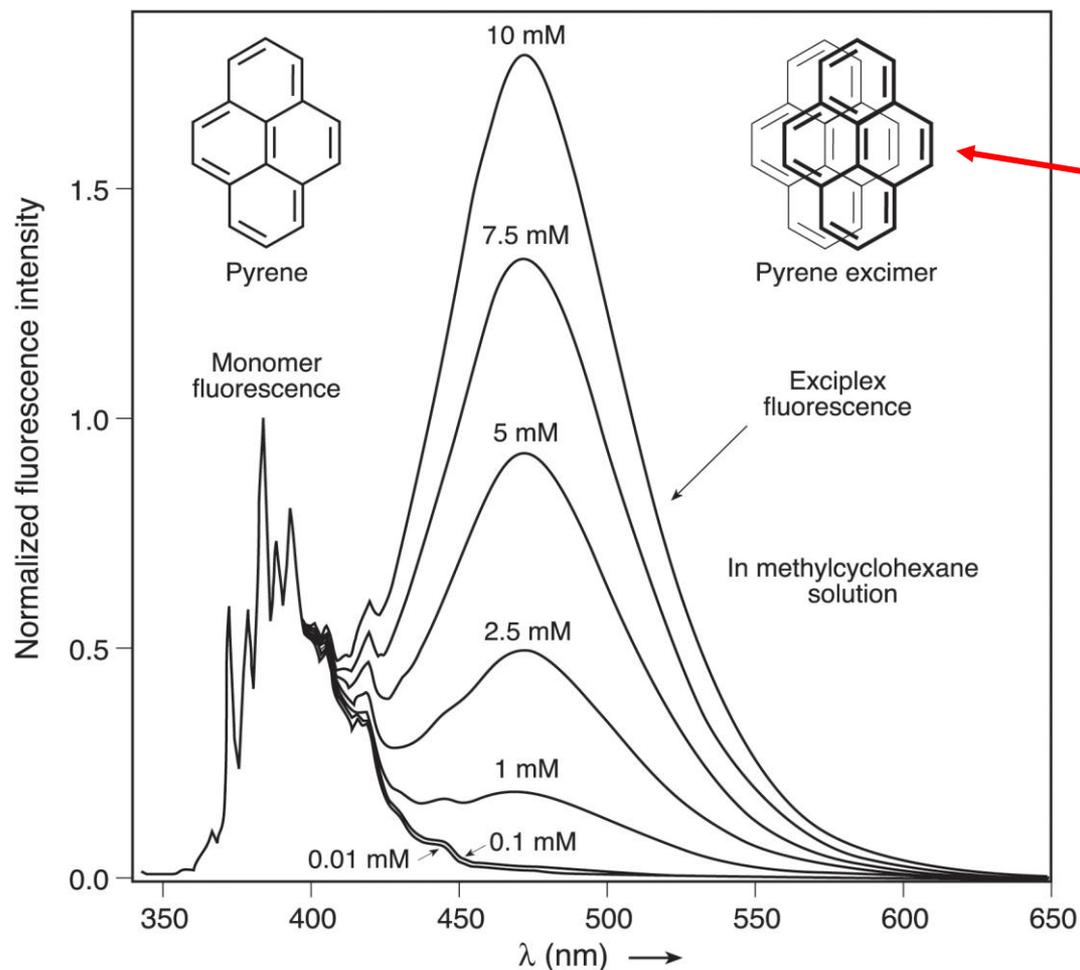
# Pyrene

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- The **pyrene excimer** is a classic example of excimer formation and emission
- At concentrations of  $\sim 10^{-5}$  M or less, the fluorescence is concentration independent and is composed of pure pyrene monomer fluorescence, which shows vibrational structure and occurs with a maximum of  $\sim 380$  nm
- As the [pyrene] increases, two effects are observed:
  - 1) A new broad, structureless fluorescence emission, due to the pyrene excimer, appears at longer wavelengths
  - 2) The relative amount of monomer emission-to-excimer emission decreases in intensity
- As the [pyrene] increases, the excimer intensity continues to increase relative to the monomer
- At [pyrene] of  $\sim 0.1$  M and greater, only excimer emission is observed

# Pyrene

- Note: The monomer emission is normalized and fixed in this figure in order to clearly demonstrate the increase in excimer emission compared to monomer emission



Experimentally concluded that the structure of the "face-to-face" pyrene singlet excimer is favored (maximum overlap of  $\pi$  orbitals)

# Pyrene

- The time dependence of emission from pyrene solutions (*time-resolved emission spectroscopy*) provides an excellent confirmation of the dynamic nature of excimer formation

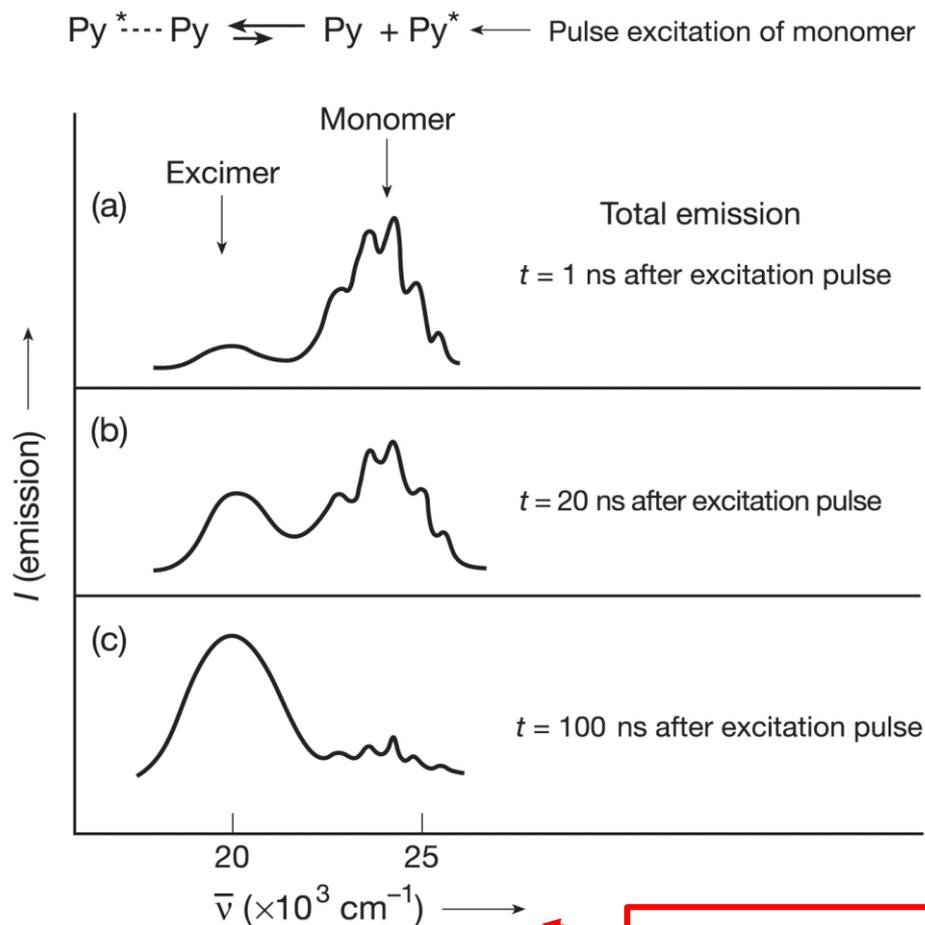


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# Exciplexes and Exciplex Emission

- As is the case for excimer emission, exciplex fluorescence emission is usually observed as a broad, structureless band at longer wavelengths relative to the monomer fluorescence emission
- The pyrene-diethylaniline system is an example of exciplex formation and emission

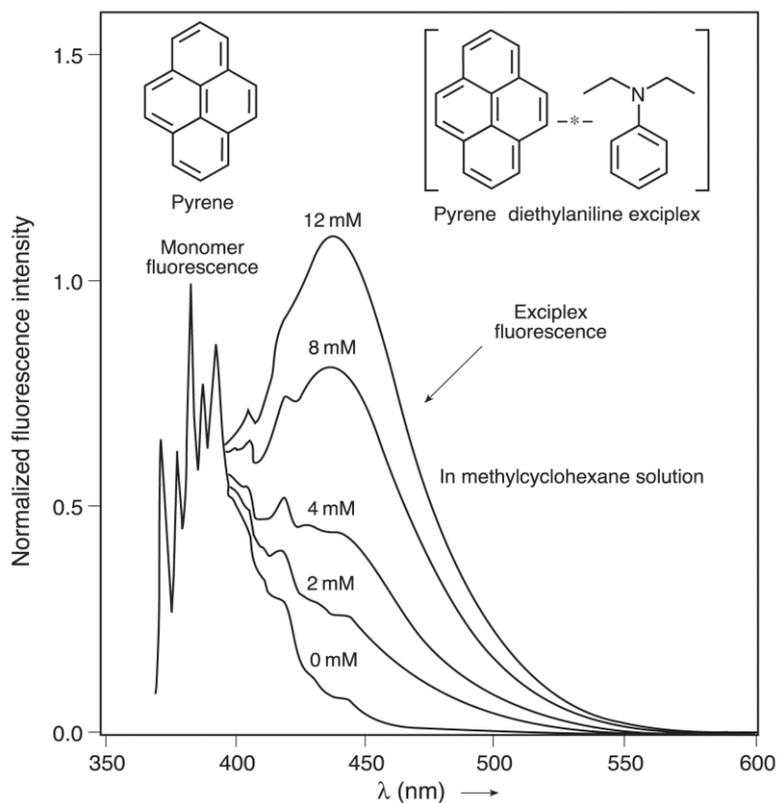


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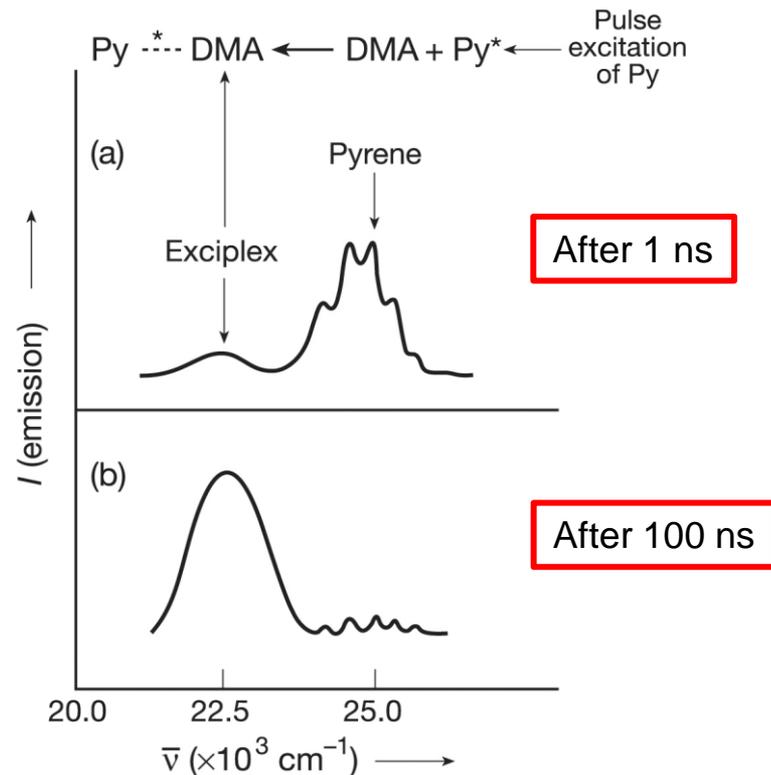


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# The Azulene Anomaly

- While fluorescence or phosphorescence is generally only observed from  $S_1$  and  $T_1$  states, respectively, because of **Kasha's rule**, there are exceptions!
- Well-documented cases of  $S_2 \rightarrow S_0 + h\nu$  fluorescence are found in **azulene** and its derivatives
- The fluorescence spectrum reaches a maximum at  $\sim 374$  nm, whereas its  $S_0 \rightarrow S_1$  absorption maximizes at 585 nm
- The 0,0 band of the fluorescence and the 0,0 band of  $S_0 \rightarrow S_2$  absorption overlap and display an approximate mirror-image relationship

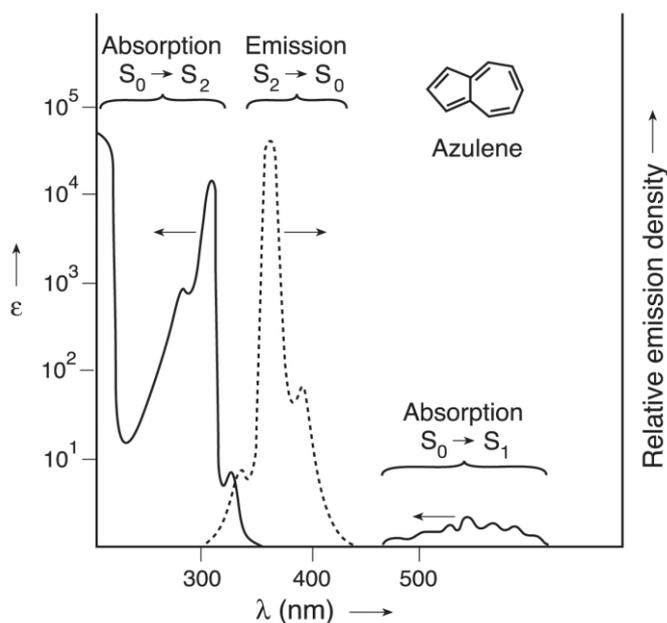


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# The Azulene Anomaly

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Question: What causes Azulene to break Kasha's rule?

- Because of its unusual molecular orbitals, the energy gap between  $S_2$  and  $S_1$  for azulene is unusually large, which slows down the normally very rapid rate of  $S_2 \rightarrow S_1$  internal conversion
- This is coupled with a fast inherent rate of  $k_F^0$  from  $S_2$
- Interestingly, the "normal"  $S_1 \rightarrow S_0$  fluorescence is extremely weak ( $\Phi_F < 10^{-4}$ )
- This is caused by the relatively small energy gap between  $S_1$  and  $S_0$ , leading to relatively fast  $S_1 \rightarrow S_0$  internal conversion

# Up Next...

**Chapter 7: Energy and Electron Transfer**