



Overview of Molecular Photochemistry

Molecular Photochemistry

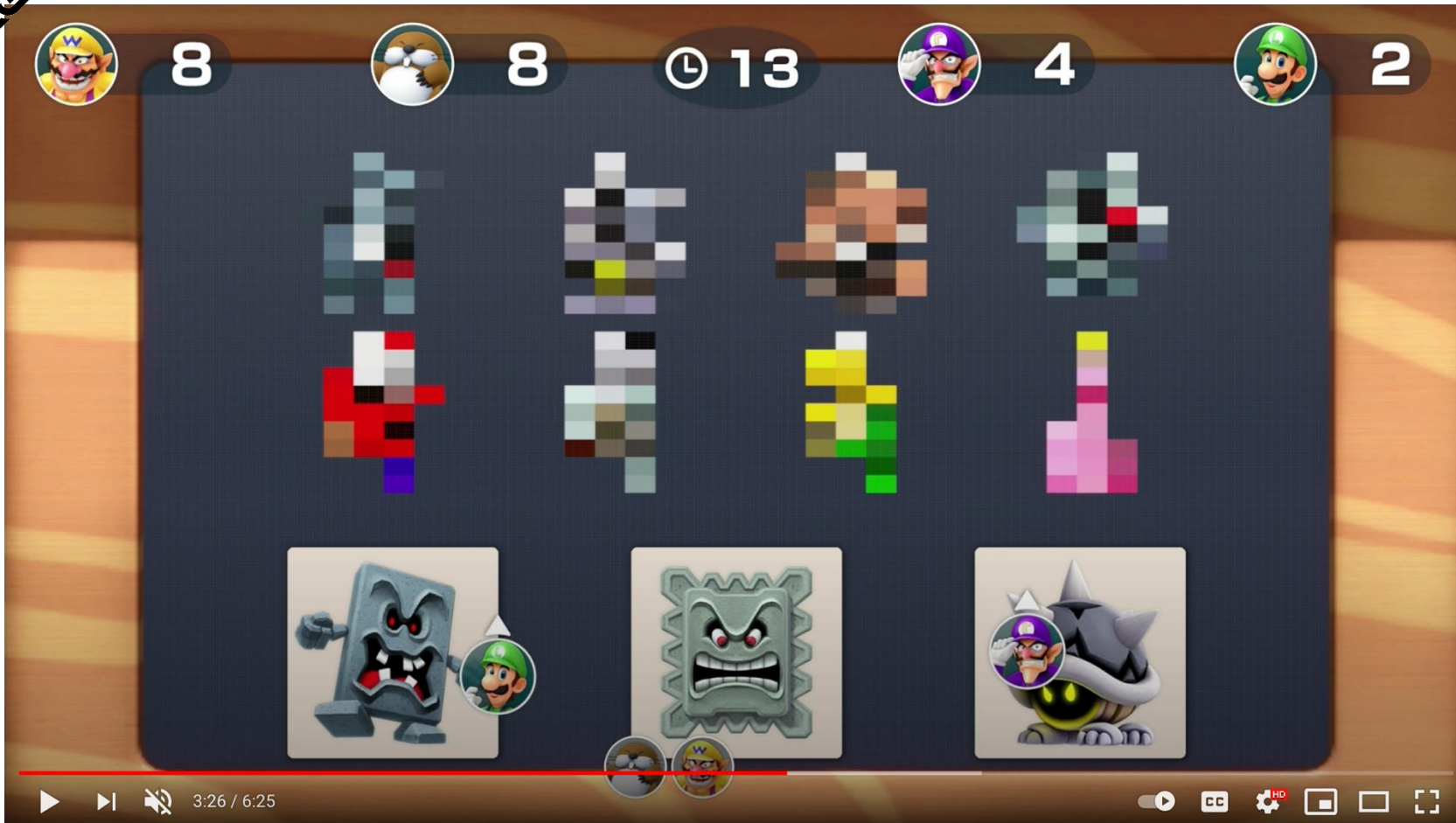
CHEM 4801

Orders of Approximation in Chemistry

Overview of Molecular Photochemistry

An Analogy: Image Resolution

As chemists we want to be able to efficiently yet robustly draw conclusions about molecular structure and properties from chemical information. We make use of various levels or ***orders of approximation*** to do this.



Zero order
“It’s Princess Peach.”

First order
“She is wearing a blue brooch.”

Second order
“Her mouth is open.”

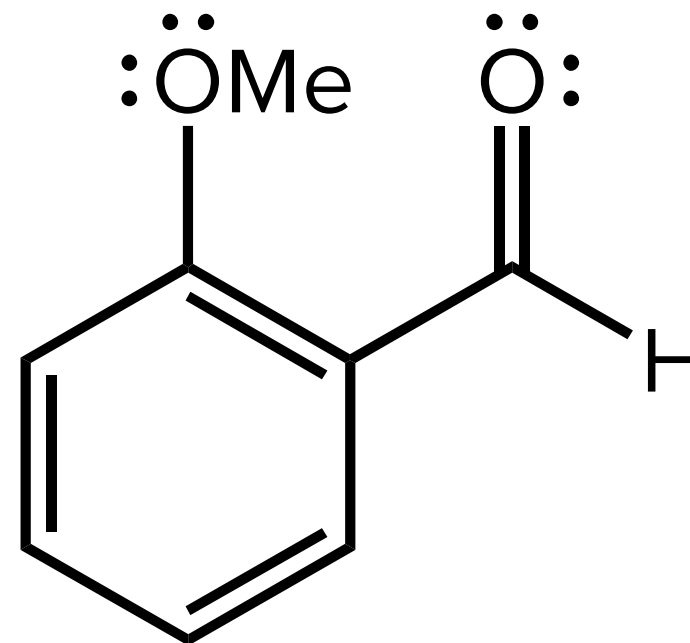
Foundational Approximations

As chemists we want to be able to efficiently yet robustly draw conclusions about molecular structure and properties from chemical information. We make use of various levels or *orders of approximation* to do this.

The Orbital Approximation, Wave Function Separability

The Born-Oppenheimer Approximation

The Lewis Structural Model; Natural Bond Orbitals



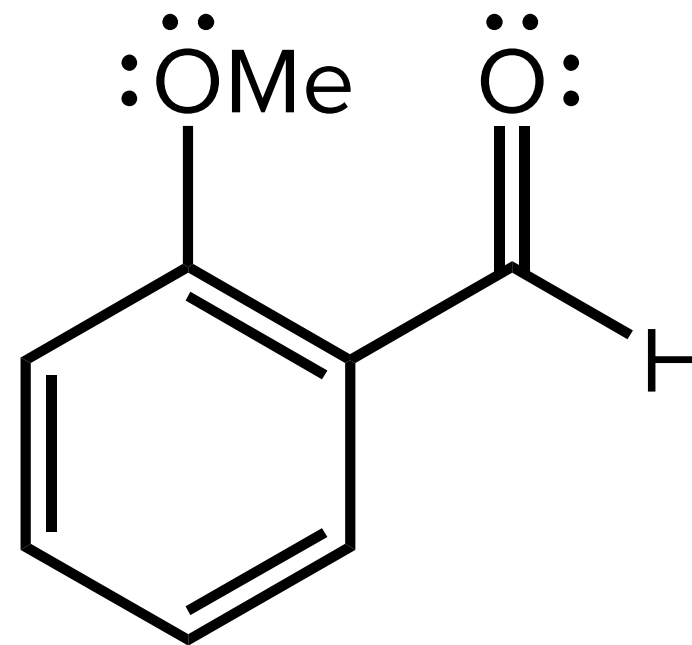
First-order Corrections

Generally "first-order corrections" mean "turning on" interactions that were ignored or disallowed at zero order.

Spin-orbit coupling

Vibronic coupling

Allowing apparently distinct quantum states to interact

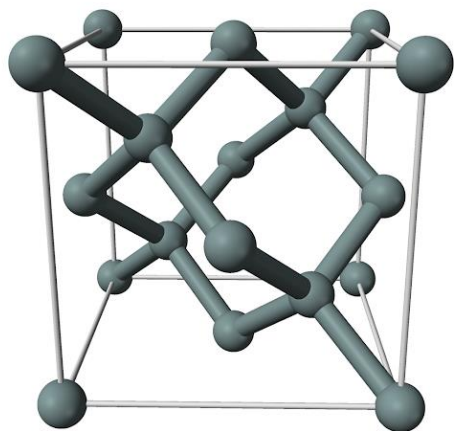


What is Molecular Photochemistry?

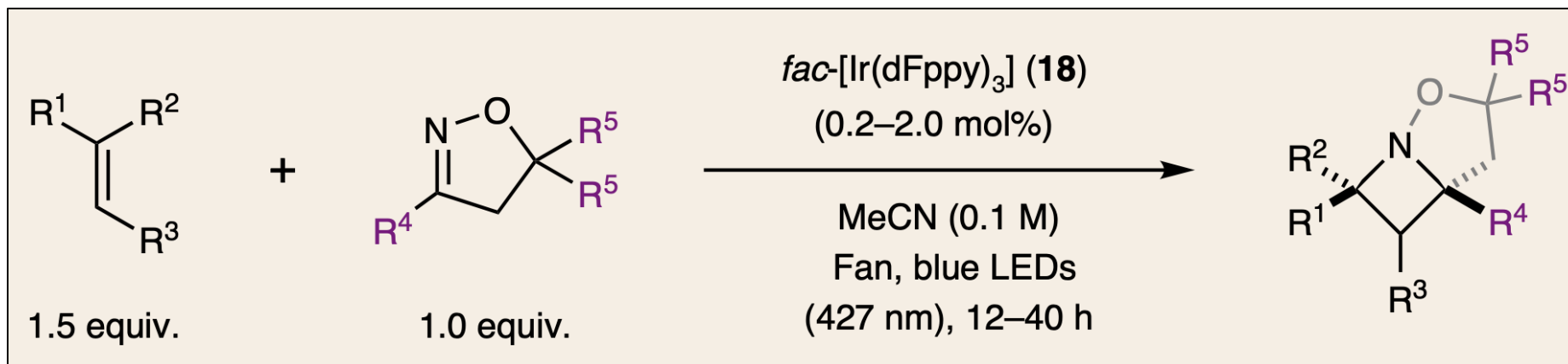
Overview of Molecular Photochemistry

Photochemistry is the study of the chemical reactions and physical changes that result from interactions between matter and visible or ultraviolet light.

What about *molecular* photochemistry?



The structures and dynamics of excited extended materials (e.g. delocalized crystals) are *not* molecular photochemistry.



Photosynthesis



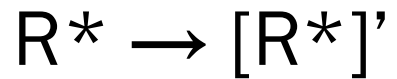
Photochemical reactions



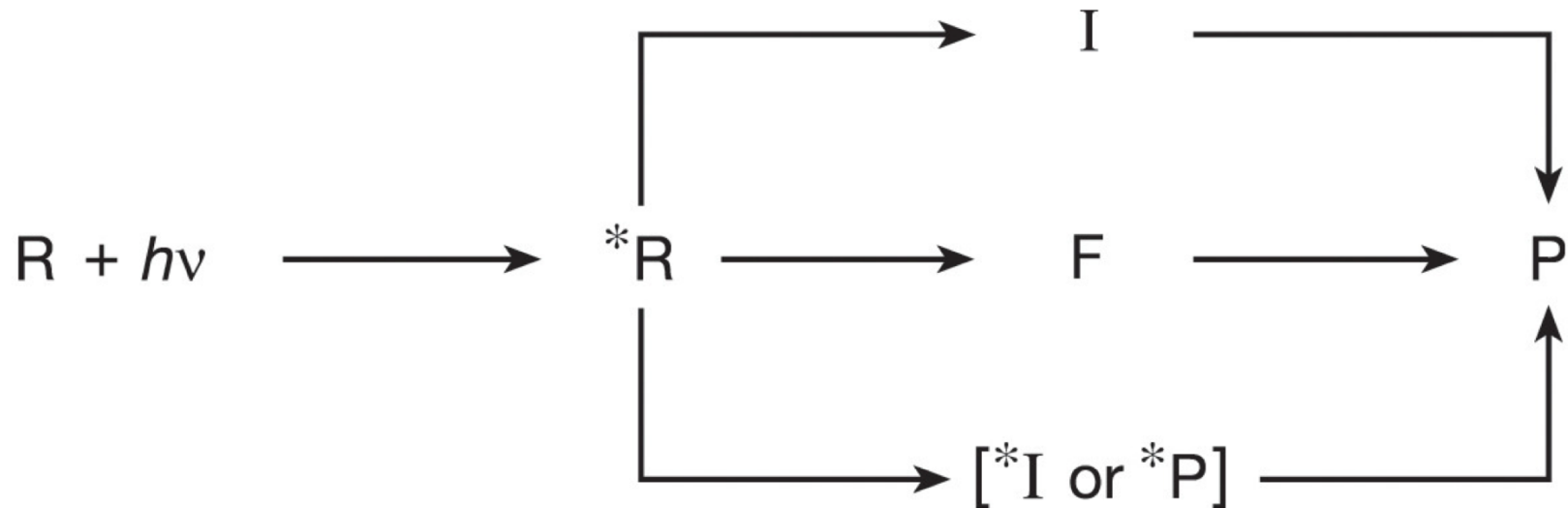
Organic photovoltaics



Photophysics: study of interactions resulting in *physical* changes



Photochemistry: study of interactions resulting in *chemical* changes

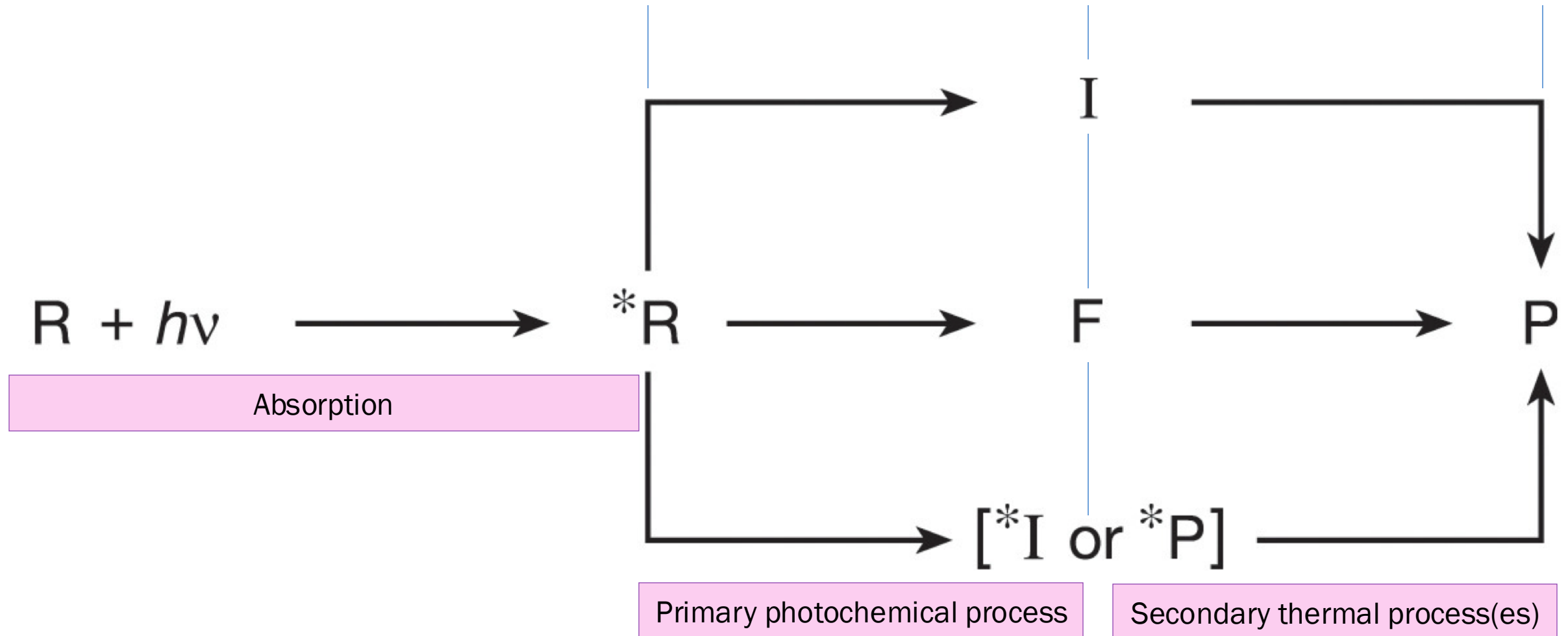


Stages of Photochemical Reactions

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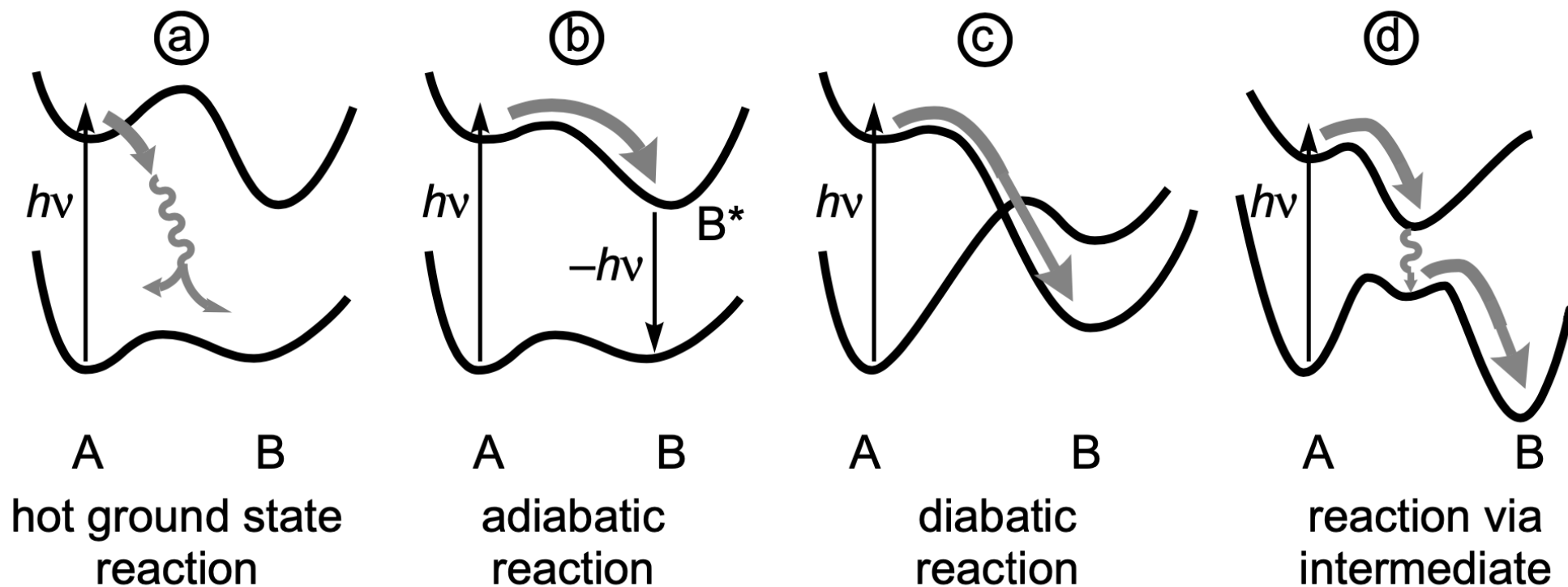
Three Photochemical Pathways

Photochemical reactions generally follow one of three possible paths. The first step is always photo-excitation (*absorption*). The *primary photochemical process* follows and *secondary thermal reactions* may then occur.



The Primary Process $*R \rightarrow F/I/P$

Primary processes involve transformation of $*R$ to a funnel, intermediate, or product. Often (not always!) this involves a movement from the excited to the ground potential energy surface.



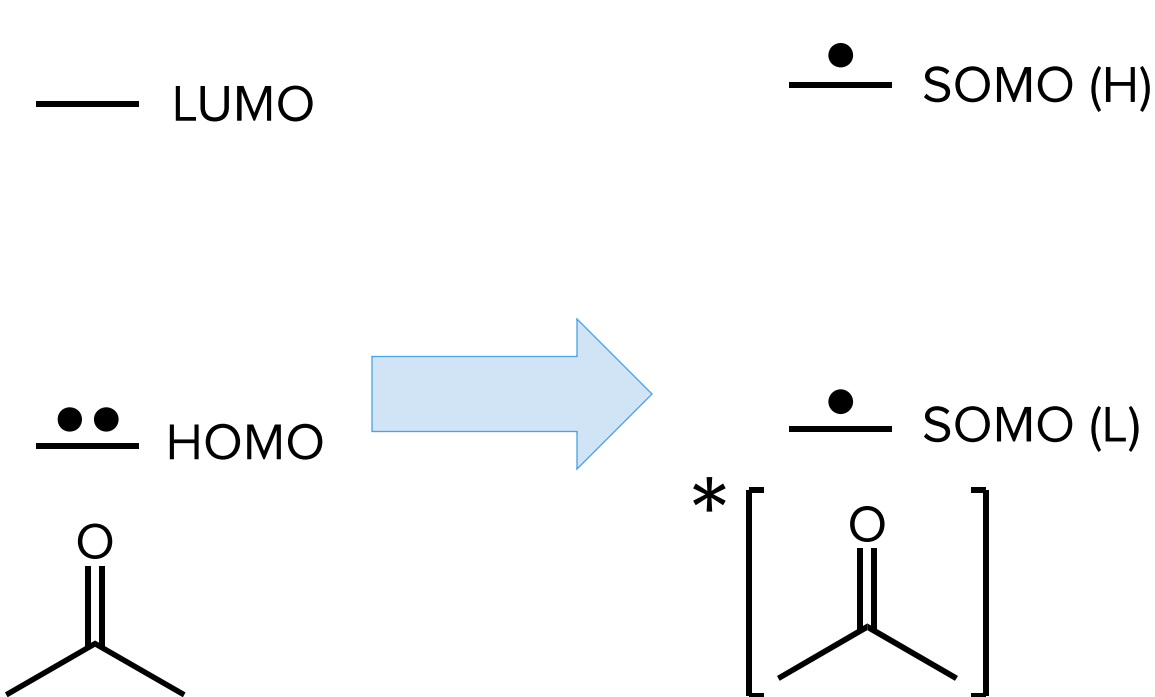
Representing Excited States, Photophysical Processes, and Photochemical Reactions

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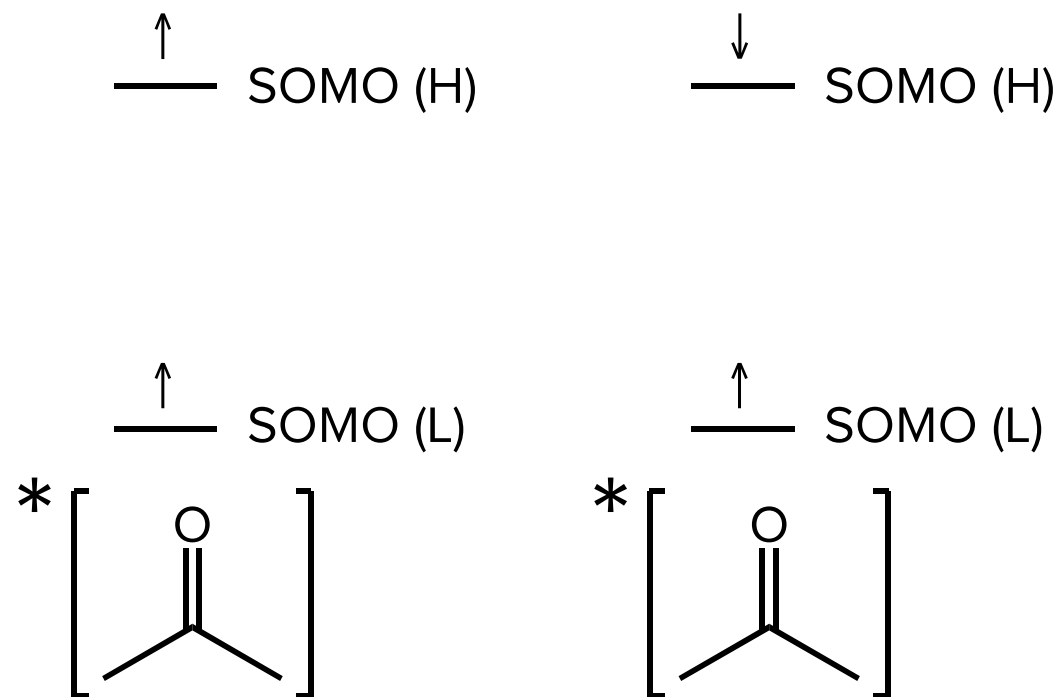
Simple Two-level Model of Excitation

Electronic excitation refers to the elevation of a molecule from a lower-energy to a higher-energy electronic state. At zero order, we can represent excitation as the elevation of an electron from a lower-energy to a higher-energy orbital (first-order corrections complicate this picture).

The excitation of lowest energy involves moving an electron from the HOMO to the LUMO.



Electron spin in the SOMOs matters a great deal for structure and reactivity.



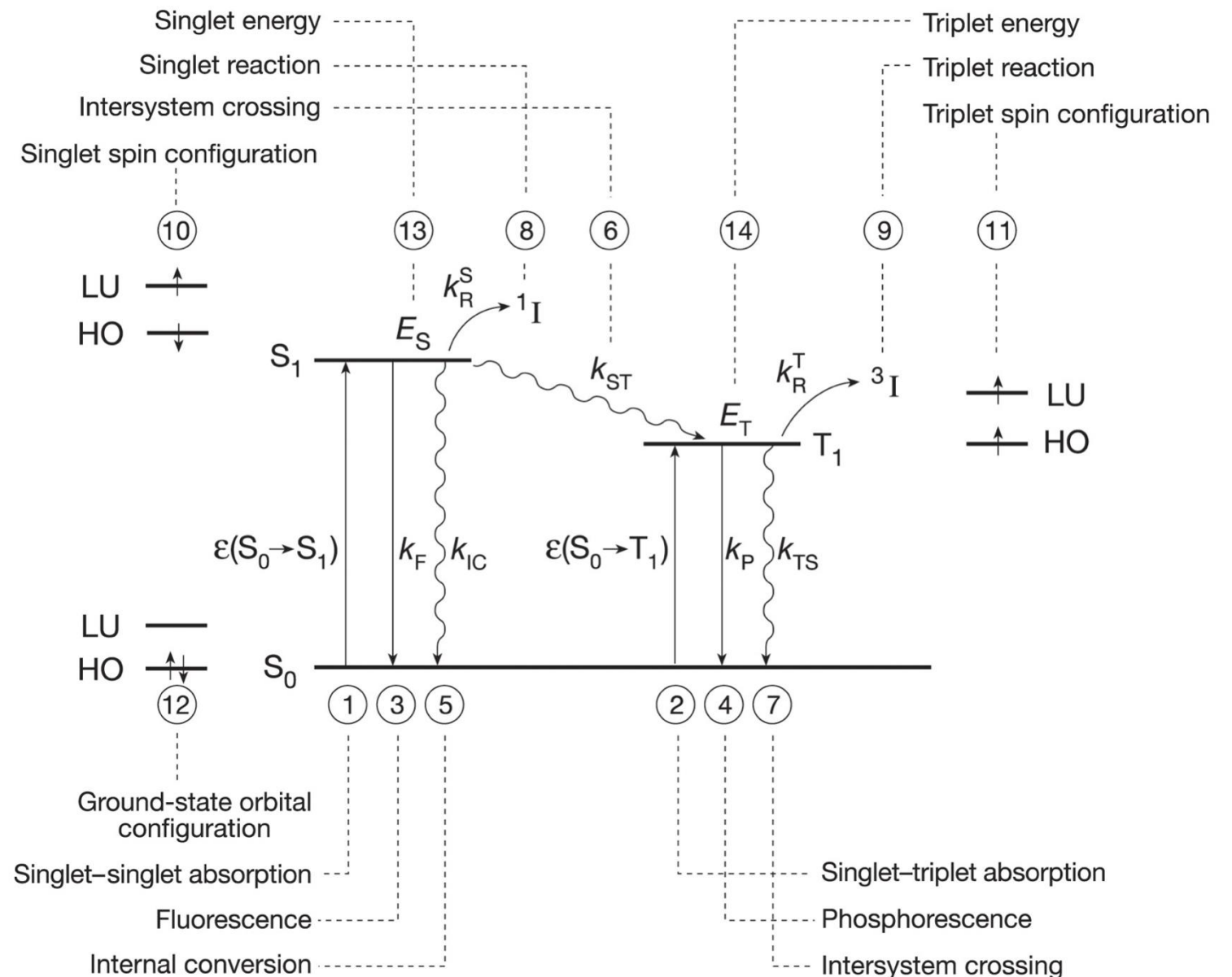
Photophysical Transitions

When an excited state changes to a different state, a **photophysical transition** takes place. The electronic, vibrational, and/or spin structure of the state changes.

Photochemical reactions involve a change in bonding.

Radiative versus **non-radiative**

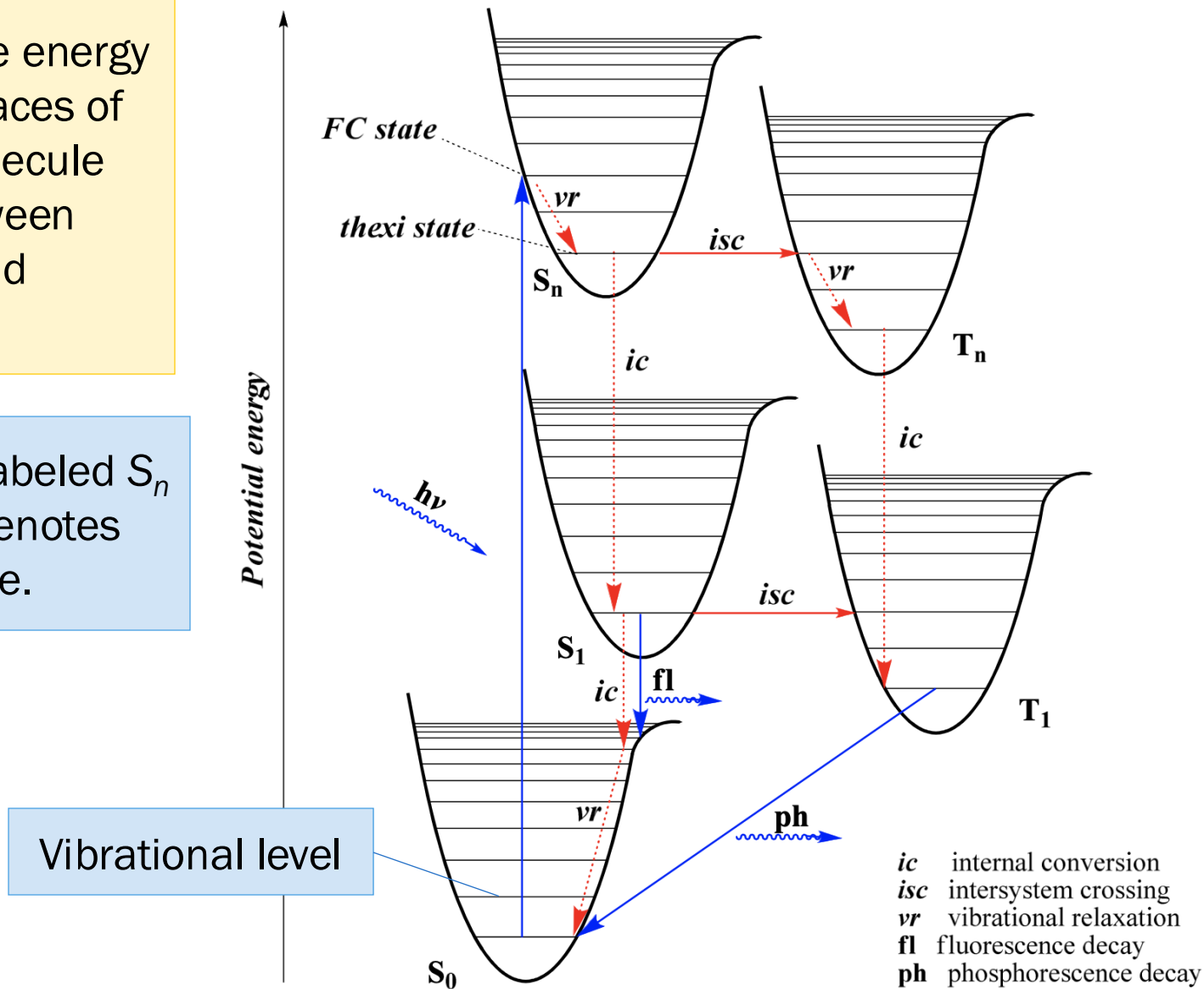
Relative rates (k values)



Jablonski Diagrams

A **Jablonski diagram** shows the energy levels or potential energy surfaces of various excited states of a molecule and (possibly) transitions between them. Here, both electronic and vibrational levels are shown.

Singlet and **triplet** states are labeled S_n and T_n respectively, where n denotes the energy ordering of the state.



Length, Time, and Energy Scales in Photochemistry

Overview of Molecular Photochemistry

Time Scales for Events of Interest

Rate (s ⁻¹)		Time (s)	Dynamic events
10 ¹⁵	femto	10 ⁻¹⁵	Electron motion Electron transfer Proton transfer
10 ¹²	pico	10 ⁻¹²	Vibrational motion Cleavage of weak bonds
10 ⁹	nano	10 ⁻⁹	Rotational and translational motion Cleavage of strong bonds Spin-orbit coupling
10 ⁶	micro	10 ⁻⁶	"Ultrafast" chemical reactions
10 ³	milli	10 ⁻³	Rotational and translational motion (large molecules or very viscous environments)
10 ⁰	–	10 ⁰	"Fast" chemical reactions
10 ⁻³	kilo	10 ³	

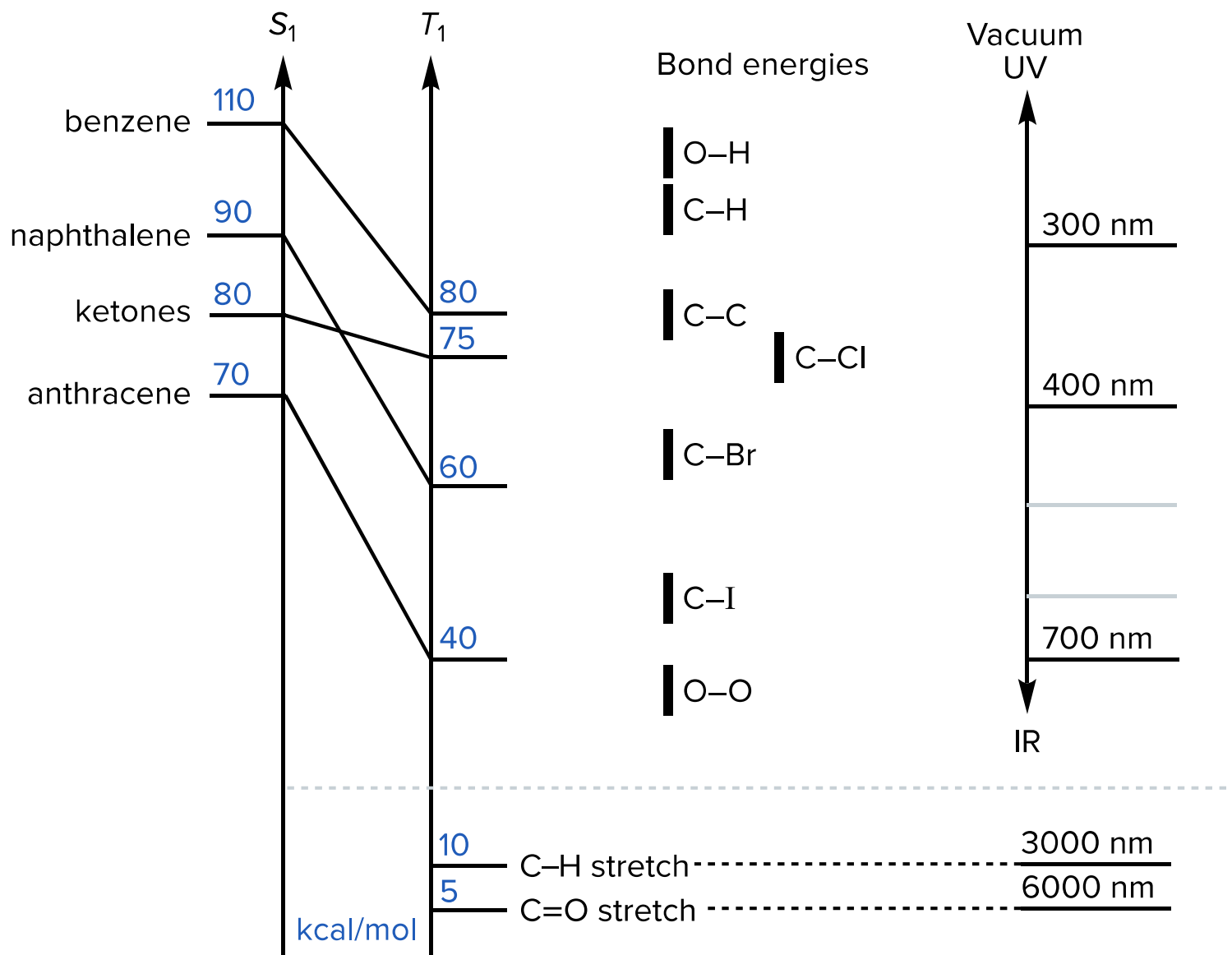
Energy Scales of Light

Region	λ		1/cm	ΔE kcal/mol	ν 1/sec	Structure and motion involved in absorption or emission
	Å	nm				
Ultraviolet	2,000	200	50,000	143.0	1.5E+15	Electrons; orbital motion
	2,500	250	40,000	114.4	1.2E+15	
	3,000	300	33,333	95.3	1.0E+15	
	3,500	350	28,571	81.7	8.6E+14	
Visible	4,000	400	25,000	71.5	7.5E+14	
	4,500	450	22,222	63.5	6.7E+14	
	5,000	500	20,000	57.2	6.0E+14	
	5,500	550	18,182	52.0	5.5E+14	
	6,000	600	16,666	47.7	5.0E+14	
	6,500	650	15,385	44.0	4.6E+14	
	7,000	700	14,286	40.8	4.3E+14	
Infrared	10,000	1,000	10,000	28.6	3.0E+14	Nuclei; vibrational motion
	50,000	5,000	2,000	5.7	6.0E+13	
	100,000	10,000	1,000	2.9	3.0E+13	
Microwave	1.00E+08	1.00E+07	10	2.9E-03	3.0E+10	Electron spin-precession
	1.00E+10	1.00E+09	0.1	2.9E-05	3.0E+08	
Radio	1.00E+12	1.00E+10	0.01	2.9E-06	3.0E+07	Nuclear spin precession

Molecular Energies: Bonds and Excited States



An intuitive sense of the relations between energy, wavelength, and wavenumber units will help you interpret photochemical results.

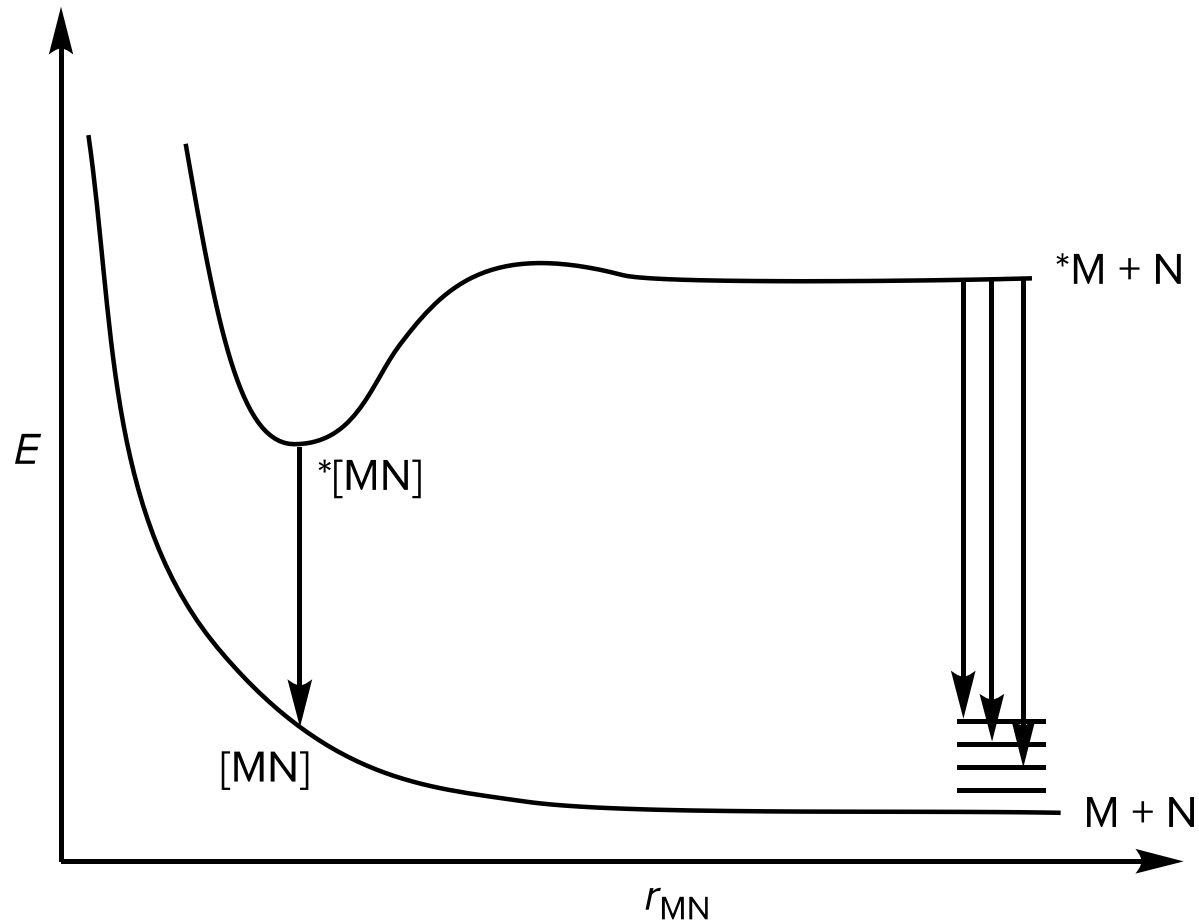


Potential Energy Surfaces in Molecular Photochemistry

Overview of Molecular Photochemistry

Potential Energy Surfaces

A **potential energy surface (PES)** shows the energy of a molecular state as a function of the nuclear coordinates. Although generally multi-dimensional, they are often reduced to two or three dimensions.



Transitions may be depicted using arrows.

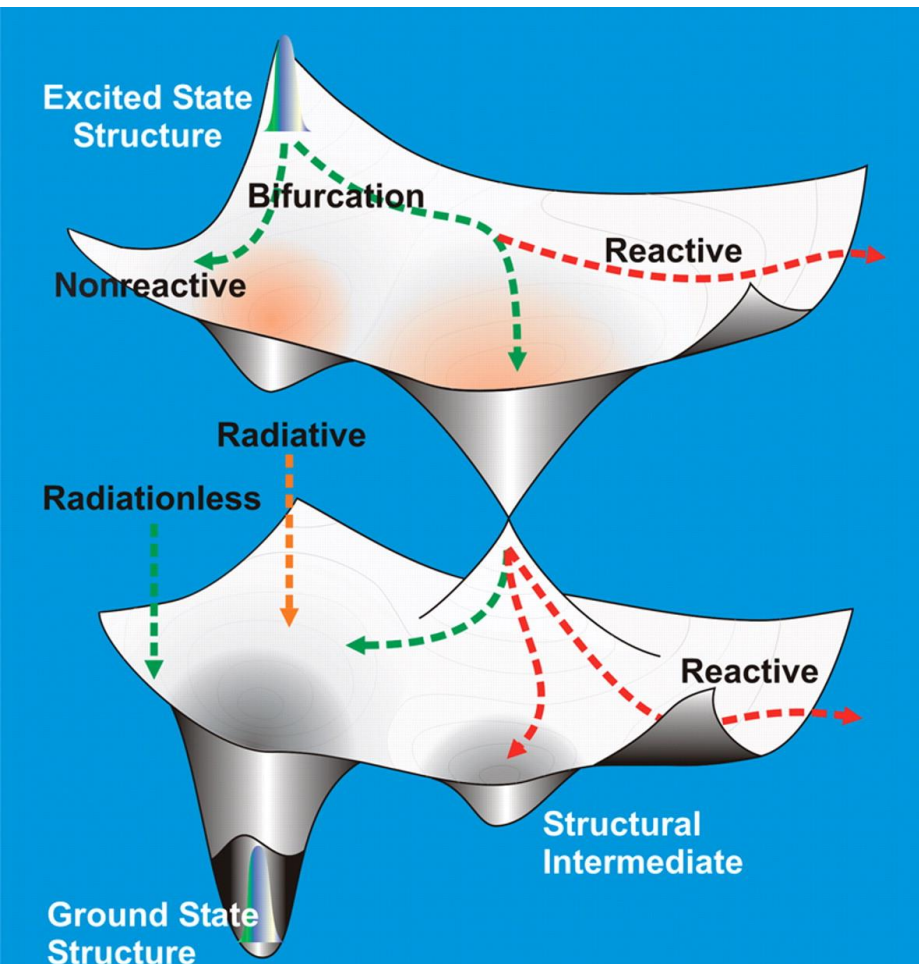
Surfaces show the *electronic* energy; distinct vibrational states also exist at each point.

The trajectory of a transition or reaction can be followed using a **representative point**.

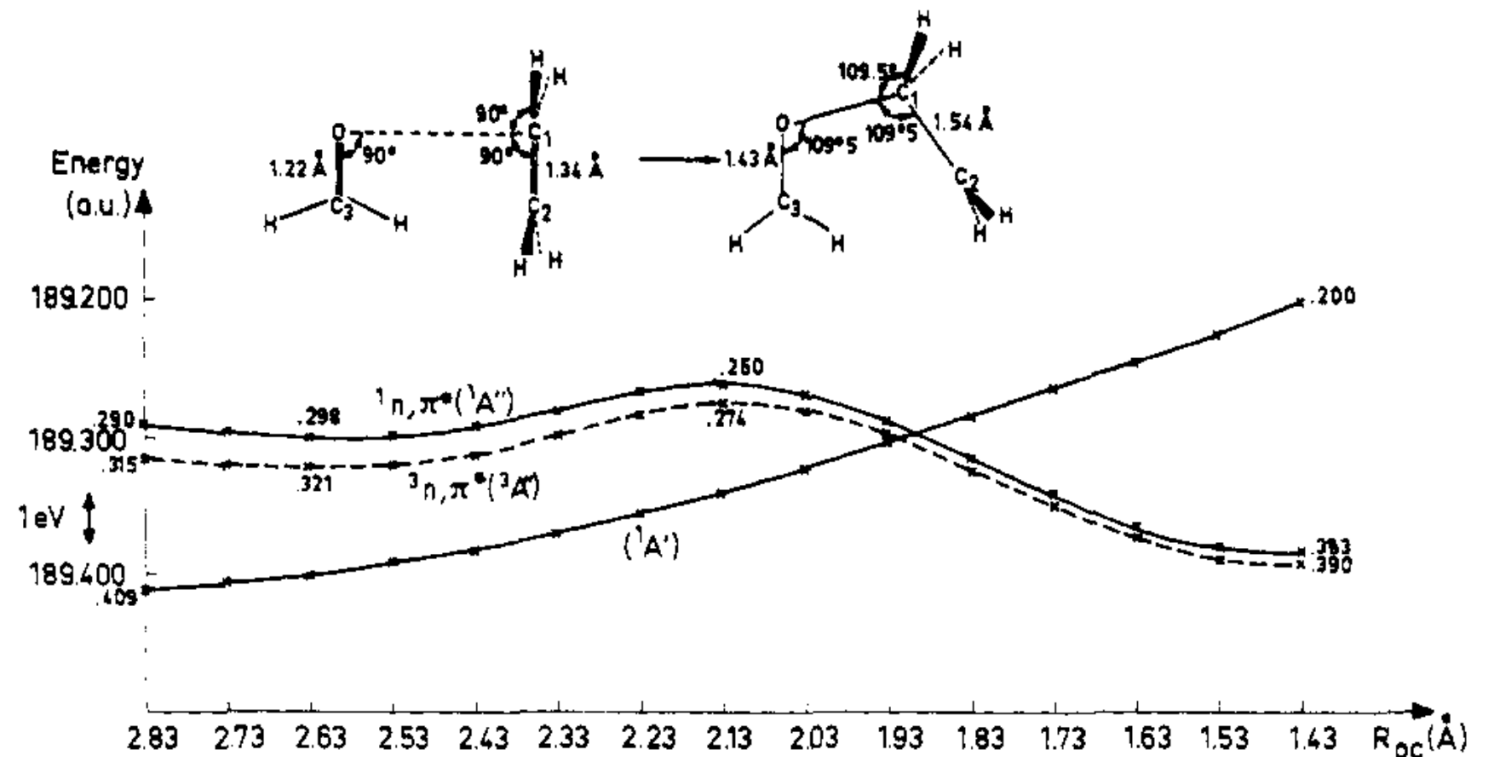
PES Structure via Experiment and Theory



Ultrafast spectroscopy and other experimental techniques, as well as quantum-mechanical and symmetry-based theories, have given us significant insight into the structures of potential energy surfaces.



Zewail, A. H. et al. *Science* 2005, 307, 558.



Salem, L. J. *Am. Chem. Soc.* 1974, 96, 3486.



Rate, Probability, and Quantum Yield

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Rate and Probability

On the quantum level, rate and probability are profoundly related. The quantum probability of a molecular-scale event is directly related to its rate: the higher the probability, the faster the rate.

$$p \propto \left| \langle \psi_f | \hat{P} | \psi_i \rangle \right|^2$$

The squared modulus of the inner product is the probability of observing a transition from ψ_i to ψ_f .

The operator P transforms the initial wave function ψ_i into a new wave function with partial ψ_f character.

Taking the inner product with $\langle \psi_f |$ gives the “amount” of ψ_f in the new wave function.

Rate and Probability

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$$p \propto \left| \langle \psi_f | \hat{P} | \psi_i \rangle \right|^2 \rightarrow k_P$$

For a unimolecular quantum process, the probability is directly related to the rate constant (units of inverse time).

Quantum Yield

Different quantum processes compete for the “action” of an excited state. *Quantum yield* (Φ) is the relative probability of observing a process given all other possible processes.

