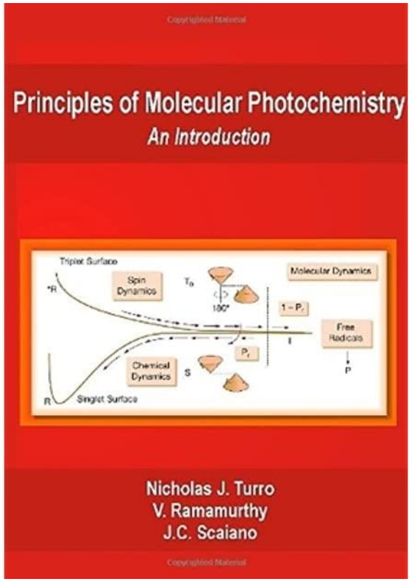
Chapter 3: Transitions between States: Photophysical Processes



Principles of Molecular Photochemistry

An Introduction

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CHEM 6420

Transitions Between States

- This Chapter will describe the *time-dependent photophysical transitions* between R and *R in which energetics and structures change with time

- Some of the transitions of interest to organic photochemists are:
  a) $R + h\nu \rightarrow {}^*R$
  b) ${}^*R \rightarrow R + h\nu$
  c) ${}^*R \rightarrow R + \text{heat}$
  d) ${}^{**}R_2 \rightarrow {}^*R_1 + \text{heat}$
  e) ${}^{**}R_2 \rightarrow {}^*R_1 + h\nu$

- <u>*Each of these transitions can involve singlet or triplet states*</u>

The Franck–Condon Principle

- In this Chapter, we are interested in the rates of transitions between an *initial* state Ψ_1 and a second state Ψ_2

- The rates of transitions between states ($\Psi_1 \rightarrow \Psi_2$) can be limited by either the rate at which electrons in Ψ_1 can adjust to the nuclear geometry of Ψ_2, or the rate at which the nuclear geometry of Ψ_1 can adjust to the nuclear geometry of Ψ_2

- The Born–Oppenheimer approximation (Chapter 2) assumes that electrons motion is so much faster than nuclear motion that the electrons “instantly” adjust to any change in the position of the nuclei in space

- Since an electron jump between orbitals generally takes ~ 10^{-15} – 10^{-16} s to occur, whereas nuclear vibrations take ~ 10^{-13} – 10^{-14} s to occur, the electron jump is much faster and will not be rate determining for transitions between two electronic states, $\Psi_1 \rightarrow \Psi_2$

The Franck–Condon Principle

- The transition rate between electronic states (of the same spin) is limited by the ability of the system to adjust to the nuclear configuration and motion after the change in electronic distribution of Ψ_1 to that of Ψ_2
- *The rate of transitions induced by vibrations (nuclear motion) depends not only on how much the electronic distributions of the initial and final states look alike but also on how much the nuclear configuration and motion in the initial and final state look alike*
- In classical terms, the Franck–Condon principle states that *because nuclei are much more massive than electrons (mass of a proton is ~ 1000 times that of an electron), an electronic transition from one orbital to another takes place while the massive, higher-inertia nuclei are essentially stationary*

James Franck
German Physicist

Edward Condon
American Nuclear Physicist

The Franck–Condon Principle

- At the instant a radiationless or radiative transition takes place between Ψ_1 and Ψ_2, the nuclear geometry of the more massive nuclei momentarily remains fixed while the new electronic configuration readjusts from that of Ψ_1 to that of Ψ_2

- After completion of the electronic transition, the nuclei experience the new electronic negative force field of Ψ_2 and begin to move and swing back and forth from the geometry of Ψ_1 until they adjust their nuclear geometry to that of Ψ_2

- From the FC principle, we conclude that the conversion of electronic energy into vibrational energy is likely the rate-determining step in an electronic transition between states of significantly different nuclear geometry (but of the same spin)

Pictures taken from Wikipedia

The Franck–Condon Principle

- Expressed in quantum mechanical terms, the FC principle states that the *most probable transitions between electronic excited states occur when the wave function of the initial vibrational state* (χ_1) *most closely resembles the wave function of the final vibrational state* (χ_2)

- In the following sections, we will demonstrate that the FC principle provides a useful visualization of both radiative and radiationless electronic transitions

- For radiative transitions, the *motions and geometries* of nuclei do not change during the time it takes a photon to “interact with” and be “absorbed”, thus causing an electron to jump from one orbital to the other

- For radiationless transitions, nuclear *motions and geometries* do not change during the time it takes an electron to jump from one orbital to another

A Model for the Frank–Condon Principle for Radiative Transitions

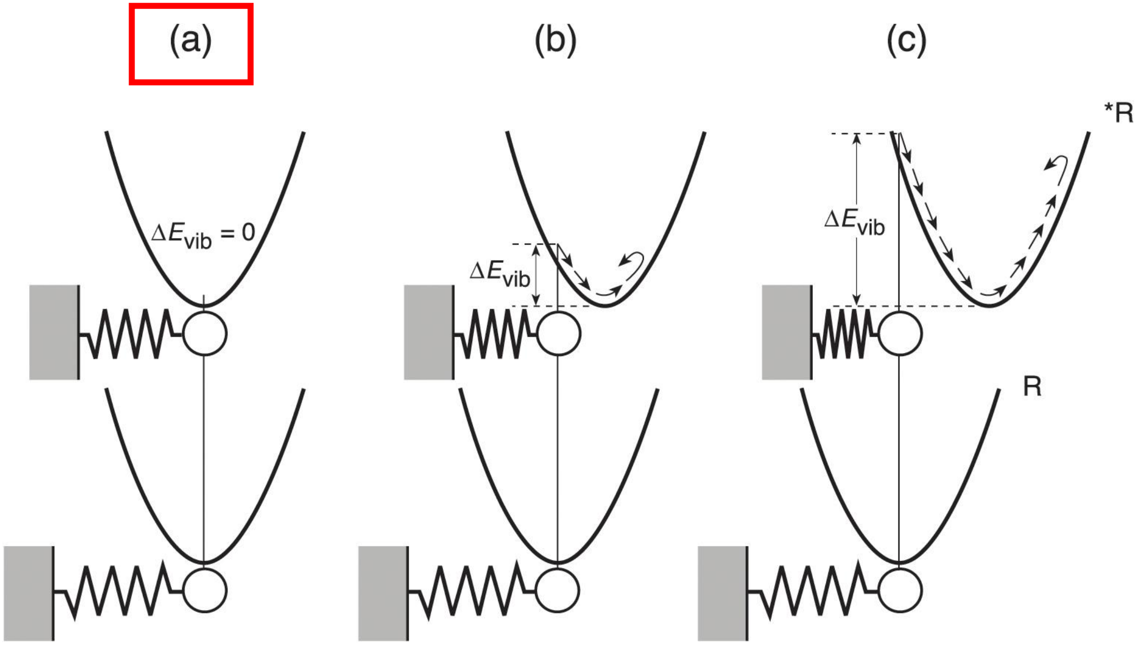
- Recap: In the classical harmonic oscillator approximation, the energies and vibrations of diatomic molecules were discussed in terms of a parabola in which the potential energy (PE) of the system was displayed as a function of the displacement (Δr) from the equilibrium separation of the atoms

- Applies to both ground states (R) and excited states (*R) and can be used as a starting point for both radiationless and radiative photophysical transitions

- Let’s now consider how the FC principle applies to a radiative transition between two states in terms of the harmonic oscillator model

A Model for the Frank–Condon Principle for Radiative Transitions

- The figure below shows three PE curves for a diatomic molecule (X–Y) that behaves as a harmonic oscillator, where X is very large (left of spring) and Y is much lighter (right of spring)
  - Analogous to a C–H bond



a) The equilibrium nuclear separation (r_{XY}) of R is essentially identical to the equilibrium nuclear separation ($^*r_{XY}$) of *R

A Model for the Frank–Condon Principle for Radiative Transitions

- The figure below shows three PE curves for a diatomic molecule (X–Y) that behaves as a harmonic oscillator, where X is very large (left of spring) and Y is much lighter (right of spring)
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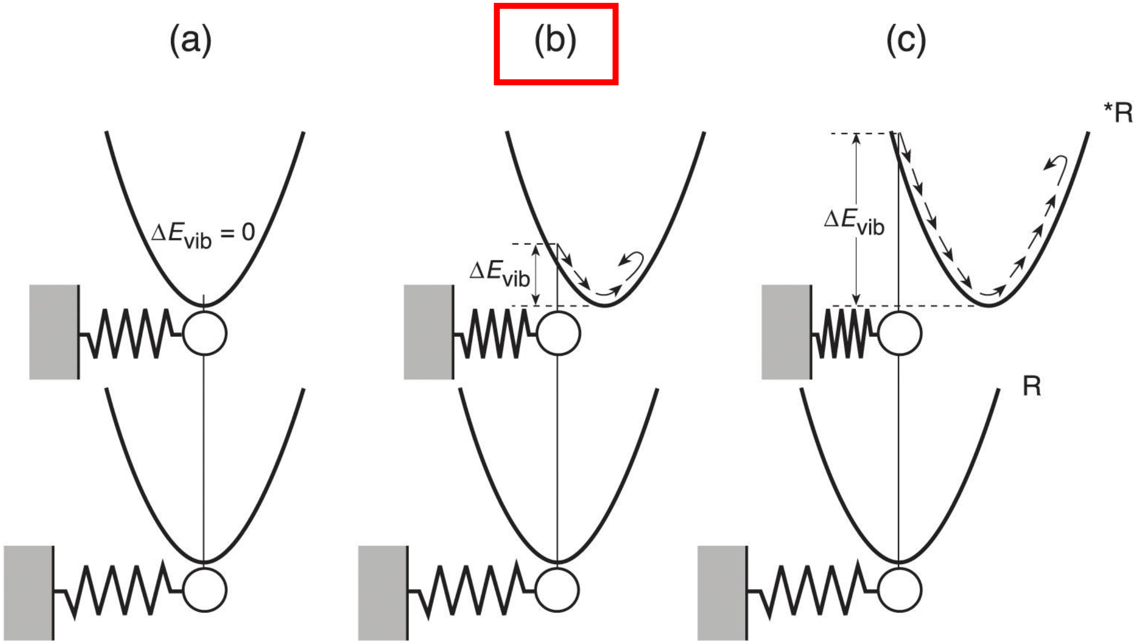

b) r_{XY} of R is *slightly* different from $*r_{XY}$ of *R, because of $*r_{XY}$ being *slightly* longer because of a slightly weaker bond resulting from electronic excitation and placement of an electron in an antibonding orbital

A Model for the Frank–Condon Principle for Radiative Transitions

- The figure below shows three PE curves for a diatomic molecule (X–Y) that behaves as a harmonic oscillator, where X is very large (left of spring) and Y is much lighter (right of spring)
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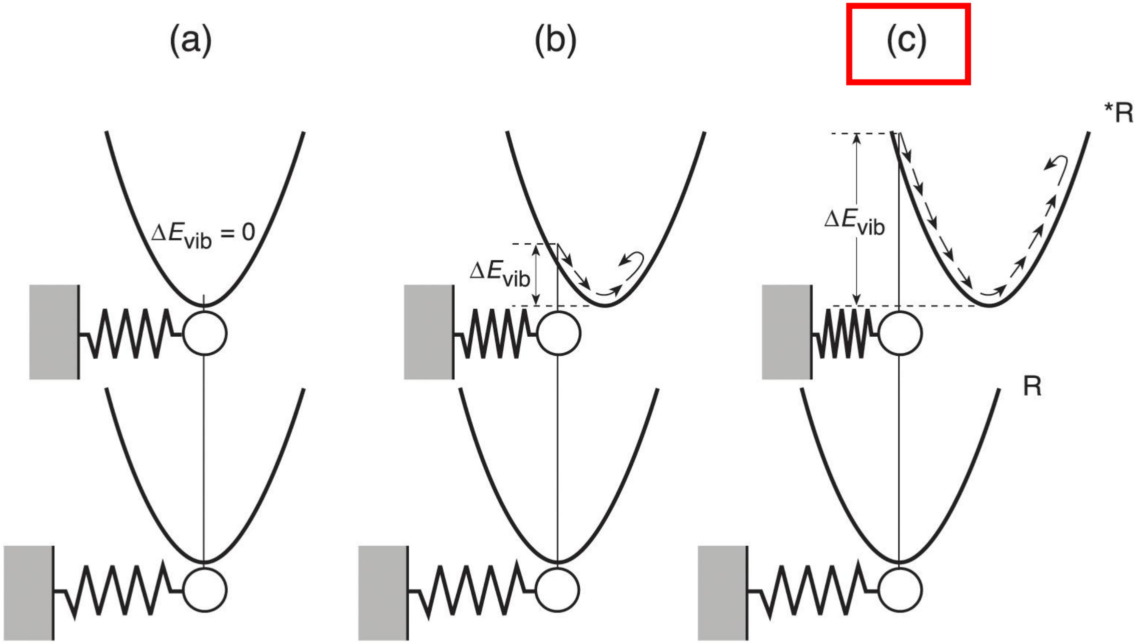
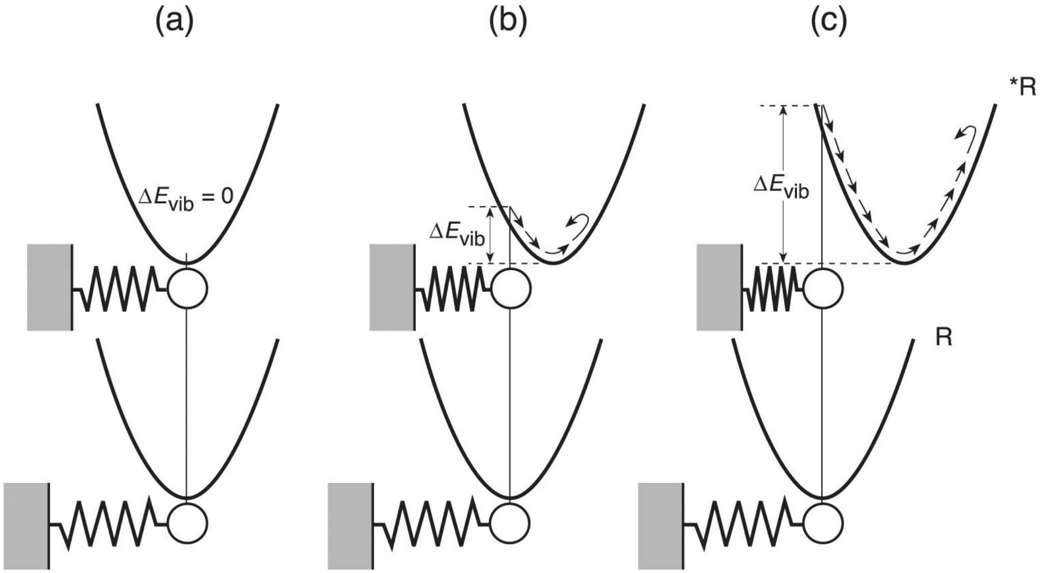


c) r_{XY} of R is *considerably* different from $*r_{XY}$ of *R, because of $*r_{XY}$ being *considerably* longer because of a much weaker bond resulting from electronic excitation and placement of an electron in an antibonding orbital

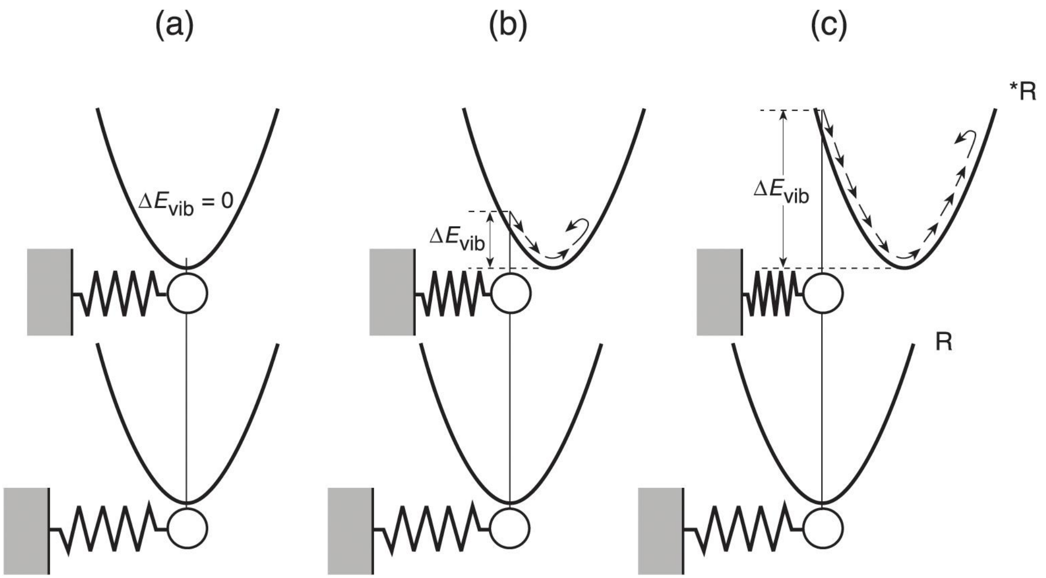
A Model for the Frank–Condon Principle for Radiative Transitions



- The difference in excess vibrational energy (ΔE_{vib}) increases as the difference in ($\Delta r = |\,{}^{*}r_{XY} - r_{XY}|$) in the equilibrium separations of R and *R increases

- It is zero in the case of (a), small for the case of (b), and large for (c)

A Model for the Frank–Condon Principle for Radiative Transitions



- For each case, a line is drawn vertically from R and intersects the upper PE curve at a point in *R. This line represents a *vertical* electronic transition from R to *R (R → *R)
- Radiative transitions are called vertical transitions with respect to nuclear geometry, since the nuclear geometry (r_{XY}, horizontal axis) is fixed during the electronic transition
- The line representing the transition corresponds to the difference in energy between R and *R that is absorbed in the transition, that is, the energy of the absorbed photon is $\left|E_R - E_{*R}\right| = \Delta E = h\nu$

A Model for the Frank–Condon Principle for Radiative Transitions

- Let's consider how the FC principle influences a radiative HO + hν → LU orbital transition that takes R to *R
- The time scale for photon absorption is on the order of 10^{-15} – 10^{-16} s
- According to the FC principle, the nuclear geometry (i.e. the separation between atoms) does not change during the time scale of an electronic transition or orbital jump
  - $r_{XY} = {}^{*}r_{XY}$ immediately after transition
- The geometry produced at the instance of the electronic transition on the upper surface by a radiative transition from R to *R is governed by the relative positions of the potential energy surfaces controlling the vibrational motion of R and *R

A Model for the Frank–Condon Principle for Radiative Transitions

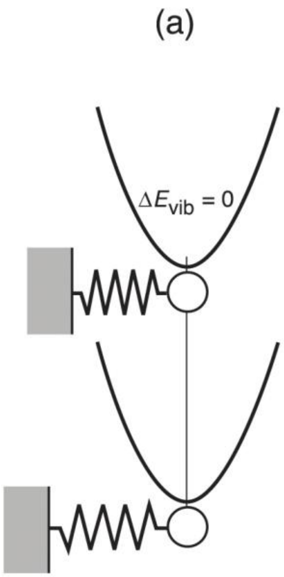
- For simplicity, let's assume the PE curves have similar shape, and the minimum of one curve lies directly over the minimum of the other [(a)]

- FC principle states most probable radiative electronic transition would be from an initial state that has separation of r_{XY} in R that is identical to r_{XY} of *R

- Since both curves are exactly over one another, the most favored FC transition will occur from the minimum of the ground state to the minimum of the excited surface

$$R(\upsilon = 0) + h\nu \rightarrow {}^*R(\upsilon = 0)$$

- Situation typical of absorption of light to induce a $\pi \rightarrow \pi^*$ transition in an aromatic hydrocarbon that has many bonding π electrons



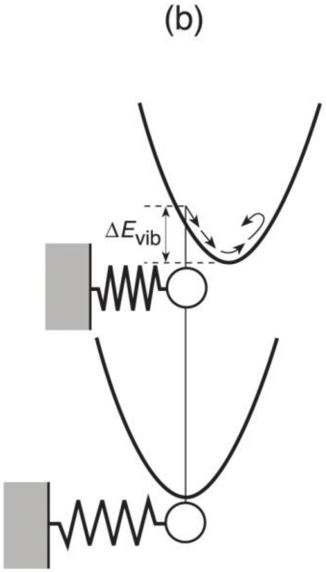
A Model for the Frank–Condon Principle for Radiative Transitions

- For (b), let’s consider the absorption of light from the HO of formaldehyde (n_O orbital) to its LU (π* orbital)

- At the instance the electronic transition is complete, the nuclei are still in the same planar geometry of the ground state

- However, as the result of the orbital transition and occupation of a π* orbital, the electron density of *R about the nuclei is different from that of R

- Therefore, *R relaxes to a new geometry (that turns out to be a pyramidally shaped $H_2C{=}O$)

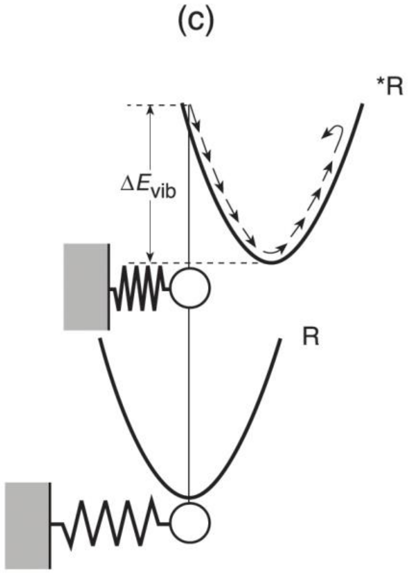


A Model for the Frank–Condon Principle for Radiative Transitions

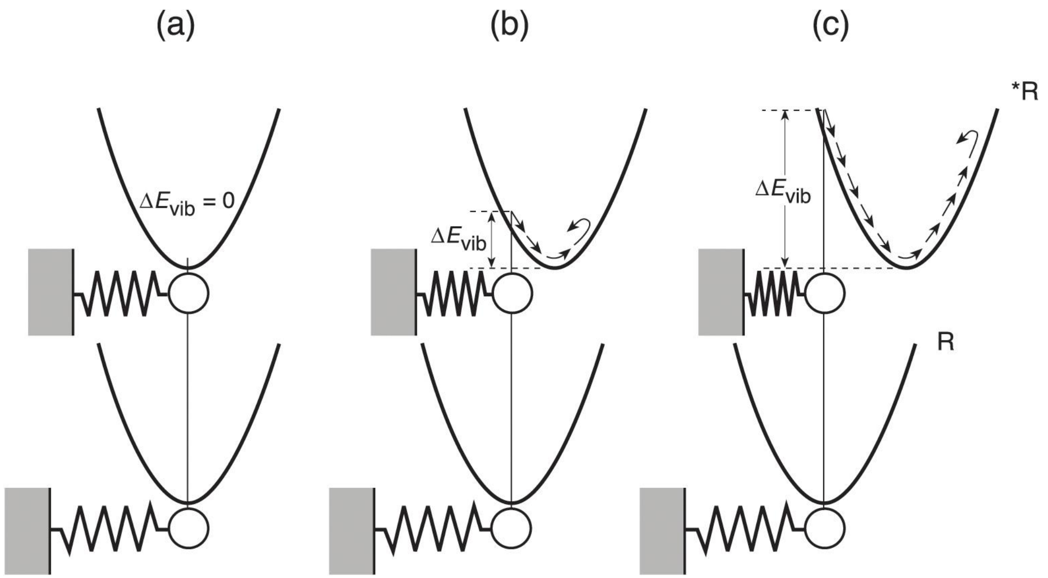
- (c) represents a system that undergoes a very large structural change upon going from R to *R

- The $\pi \rightarrow \pi^*$ of ethylene is such an example

- Although the ground state equilibrium geometry of ethylene (R) is planar, the equilibrium geometry of the excited state for ethylene (*R) is strongly twisted, leading to a large change in the equilibrium geometry of *R vs. R

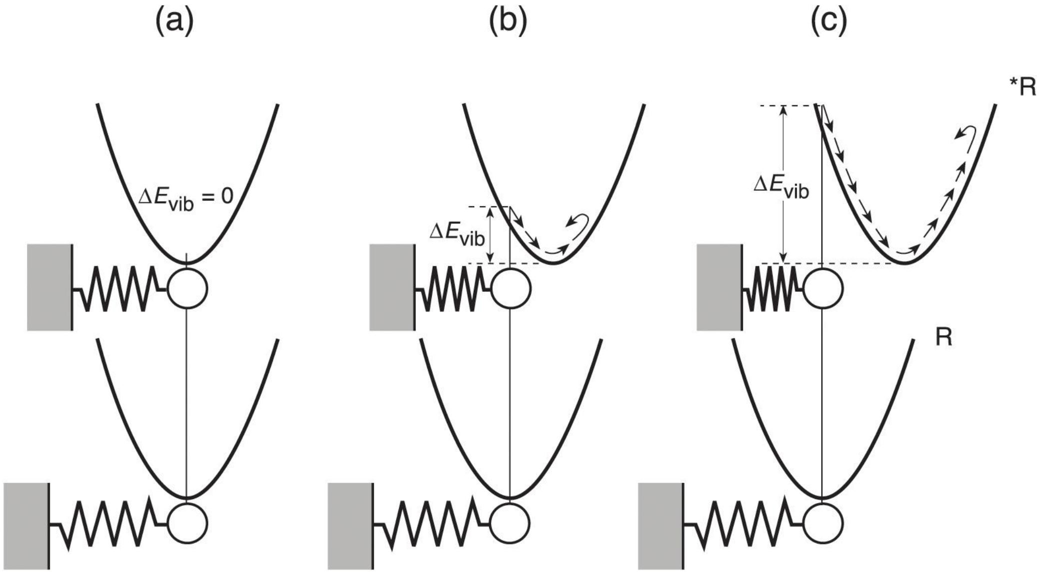


A Model for the Frank–Condon Principle for Radiative Transitions



- For (a), the initial and final geometries of R and *R are assumed to be identical, there is no significant change in the vibrational properties resulting from electronic excitation, so *R is produced with no excess vibrational energy
- In both (b) and (c), the electronic transition produces an *R state that is both a *vibrationally excited and an electronically excited species*
- A few fs after the R → *R transition, the atoms will burst into new vibrational motion in response to the new electronic force field of *R

A Model for the Frank–Condon Principle for Radiative Transitions



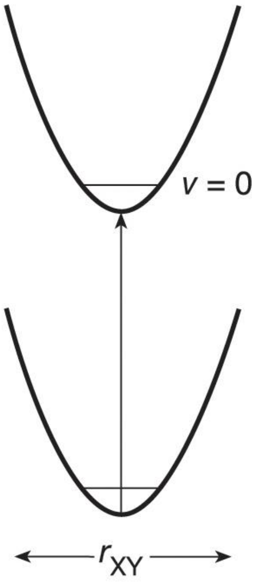
- In the case of the n,π* state of formaldehyde (b), an electron is promoted into the π* orbital, which will tend to make the C–O bond vibrate and stretch and become longer
- In the case of the $\pi \rightarrow \pi$* transition of ethylene (c), the loss of a π electron and the creation of a π* electron strongly reduces the C=C bonding and essentially breaks the π bond, and creates a C–C single bond in *R
- This new electronic distribution favors a twisting around the C–C single bond and an equilibrium geometry that favors two CH_2 groups perpendicular to each other rather than on the same plane

A Model for the Frank–Condon Principle for Radiative Transitions

- The classical PE curves are now replaced by PE curves displaying the quantized vibrational levels, each with a vibrational quantum number, υ

- The figure below shows the ground state PE curve with a horizontal level corresponding to $\upsilon = 0$ vibrational level. This level corresponds to a small range of nuclear geometries

- *Radiative transitions from* $\upsilon = 0$ *will therefore not be initiated from a single geometry but from a range of geometries that are explored in the zero-point motion of the vibration*



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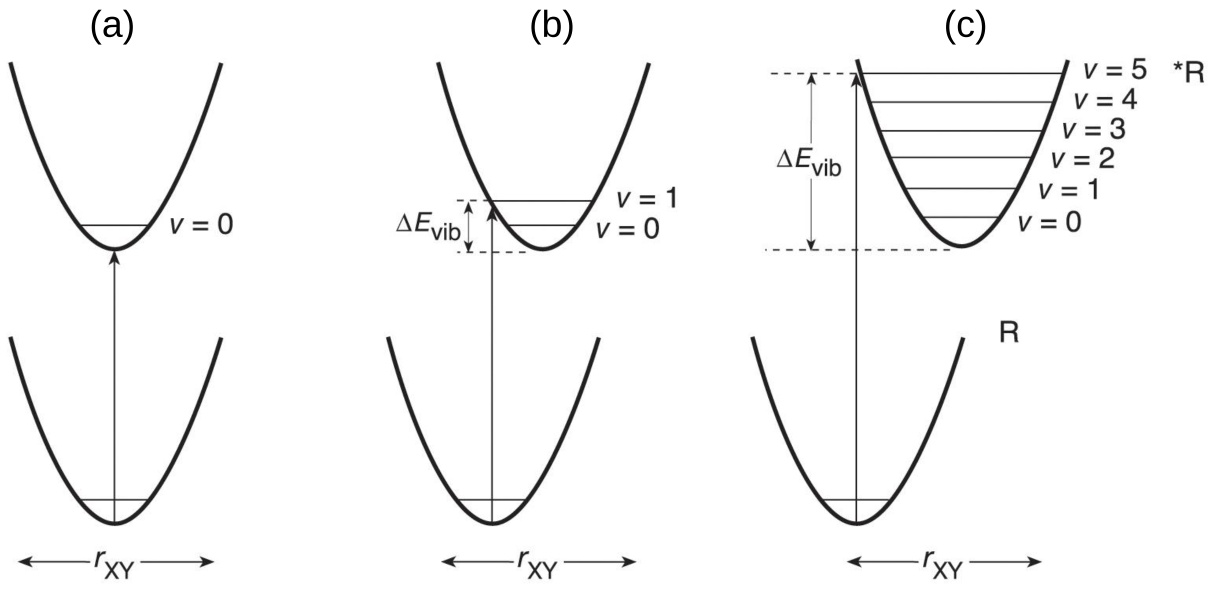
A Model for the Frank–Condon Principle for Radiative Transitions

- For (a), the most probable transition is from the $\upsilon = 0$ level of R to the $\upsilon = 0$ level of *R
- For (b), the most probable transition is from the $\upsilon = 0$ level of R to the $\upsilon = 1$ level of *R
- For (c), the most probable transition is from the $\upsilon = 0$ level of R to the $\upsilon = 5$ level of *R
- As we go from (a) – (c), the amount of excess vibrational energy produced in *R by the electronic transition increases



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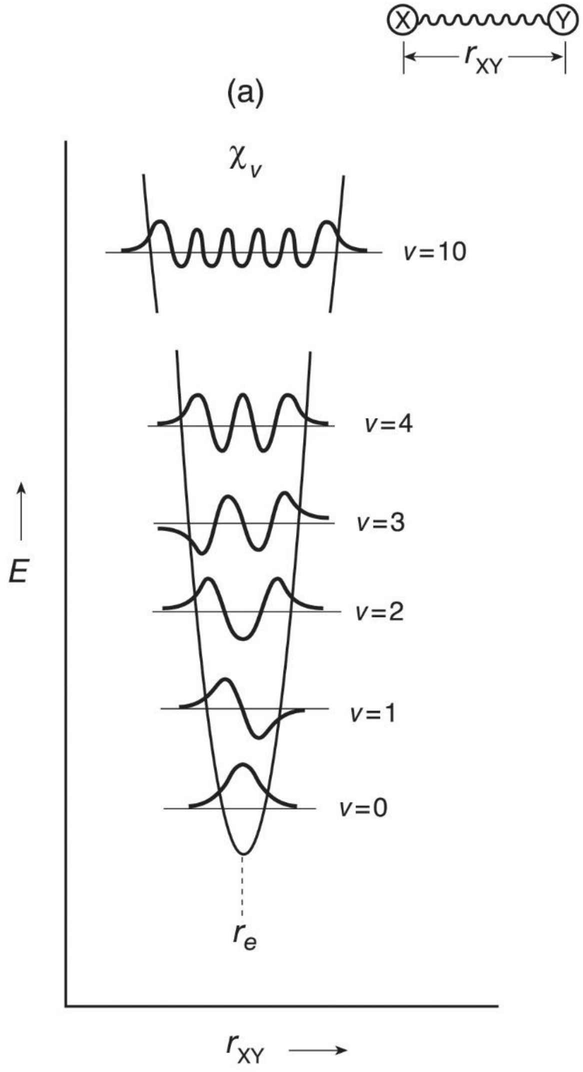
A Quantum Mechanical Interpretation

- Recap: Vibrational wave function, χ: Describes the nuclear configuration and nuclear vibrational momentum during a vibration
- In the language of *classical mechanics*, the FC principle states that the most probable electronic transition will occur between those states possessing similar nuclear configuration and vibrational momentum at the instant of an electronic transition
- In the language of *quantum mechanics*, the FC principle states that the most probable electronic transitions are those that possess vibrational wave functions that look most alike in the initial (χ_1) and final (χ_2) states at the instant of the electronic transition



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A Quantum Mechanical Interpretation

- Franck-Condon Factor: measure of the overlap of the vibrational wave functions of the initial and final states

- The larger the FC factor, the greater the overlap of the vibrational wave functions, the more similar χ_1 is to χ_2, the more probable the transition

- The FC factor may be considered a sort of nuclear “reorganization energy”, similar to entropy, that is required for an electronic transition to occur

- The greater the reorganization energy, the smaller the FC factor and the slower the electronic transition

- The smaller the reorganization energy, the larger the FC factor and the more probable the electronic transition

A Quantum Mechanical Interpretation

- The FC principle provides a selection rule for the *relative probability of vibronic transitions*

- Qualitatively, for *radiative* transitions of absorption or emission the FC factor *governs* the relative intensities of the vibrational bands in electronic absorption and emission spectra

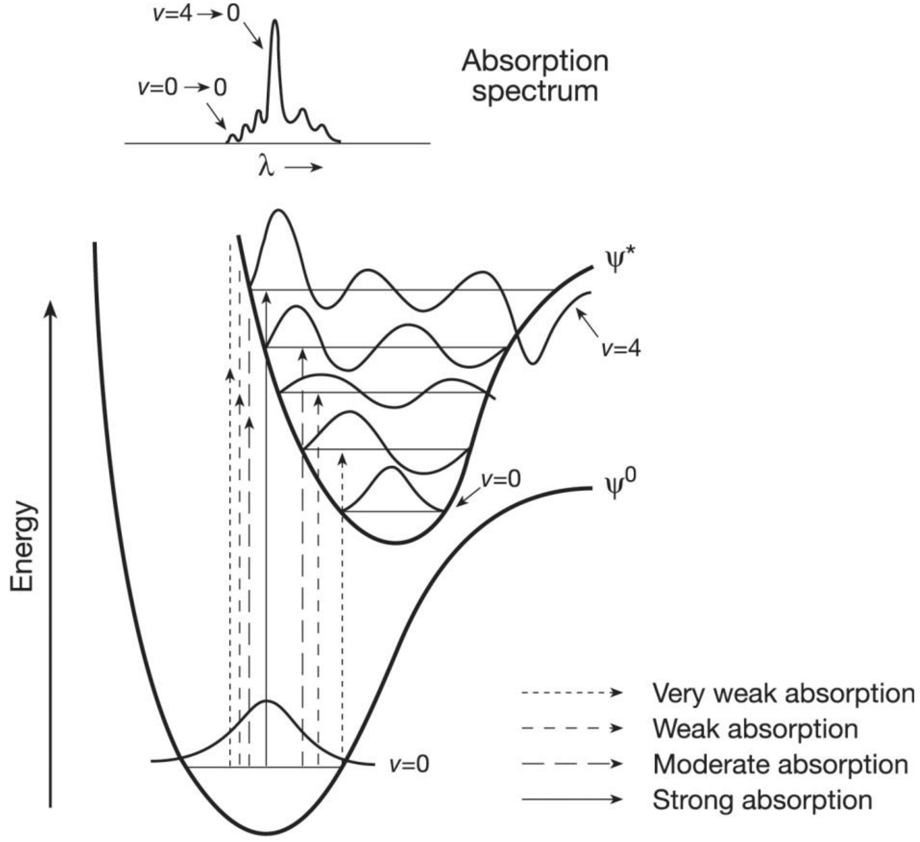
- The larger the difference for χ_1 compared to χ_2, the more likely it is that the equilibrium shape and/or momentum of the initial and final states are different, and the more difficult and slower and less probable the transition $\chi_1 \rightarrow \chi_2$

A Quantum Mechanical Interpretation

- A schematic representation of the quantum mechanical basis of the FC principle for a radiative transition from an initial ground excited state Ψ^0 (i.e. R) to a final electronic excited state Ψ^* (i.e. *R)

- Absorption of a photon is assumed to start from the lowest energy, $\upsilon = 0$ of Ψ^0 since it is usually the most populated level of R

- The most likely radiative transition from $\upsilon = 0$ of Ψ^0 to a vibrational level of Ψ^* corresponds to a vertical transition for where the overlap is maximal



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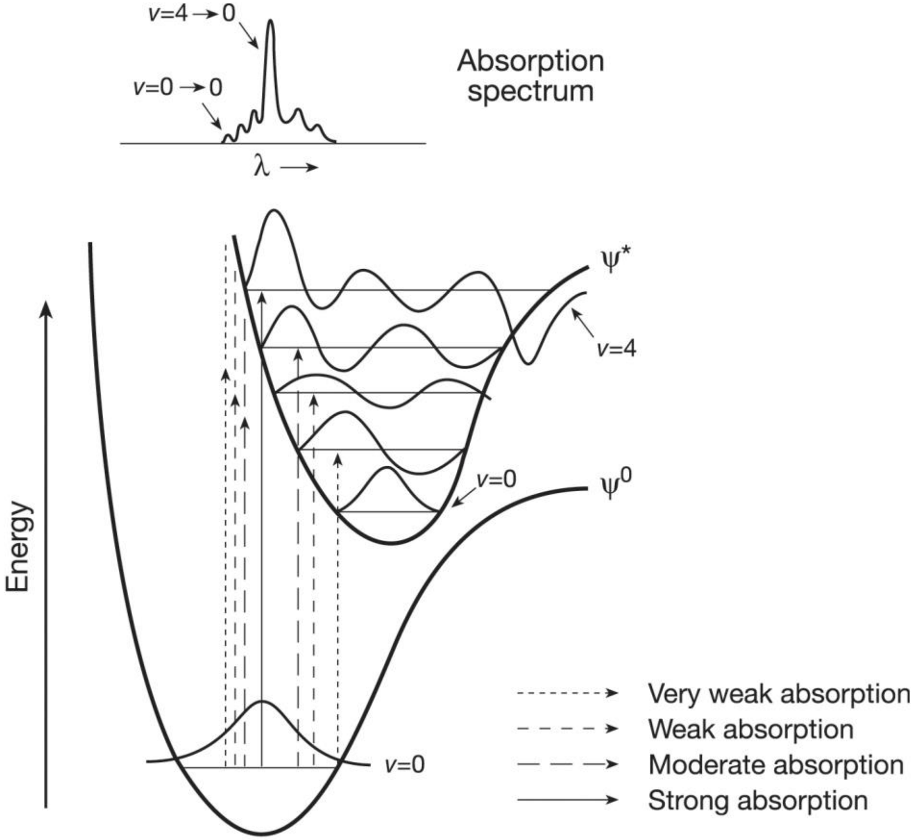
A Quantum Mechanical Interpretation

- By inspection, it is maximal for the $\upsilon = 0 \rightarrow \upsilon = 4$ transition

- Transitions to other vibrational levels may occur, but with lower probability

- A possible resulting absorption spectrum showing schematically how the intensities would vary is shown above the PE curves

- *<u>The same ideas apply to emission</u>*, except now the important overlap is between the χ of $\upsilon = 0$ of Ψ^* and the various vibrational levels of Ψ^0



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The Franck–Condon Principle for Radiationless Transitions

- The classical and quantum mechanical ideas behind the FC principle for *radiative* transitions can be extended to *radiationless* transitions

- The basic idea is the same; namely,
  1) A small change in the initial and final nuclear structure and momentum is favored
  2) Energy must be conserved during the transition

- For radiative transitions, energy is conserved during a transition by the absorption or emission of a photon (hν), which corresponds exactly to the energy difference between the initial and final states

- For a radiationless transition, <u>*the initial and final electronic states must have the same energy and the same nuclear geometry*</u>
  - Must look alike energetically and structurally

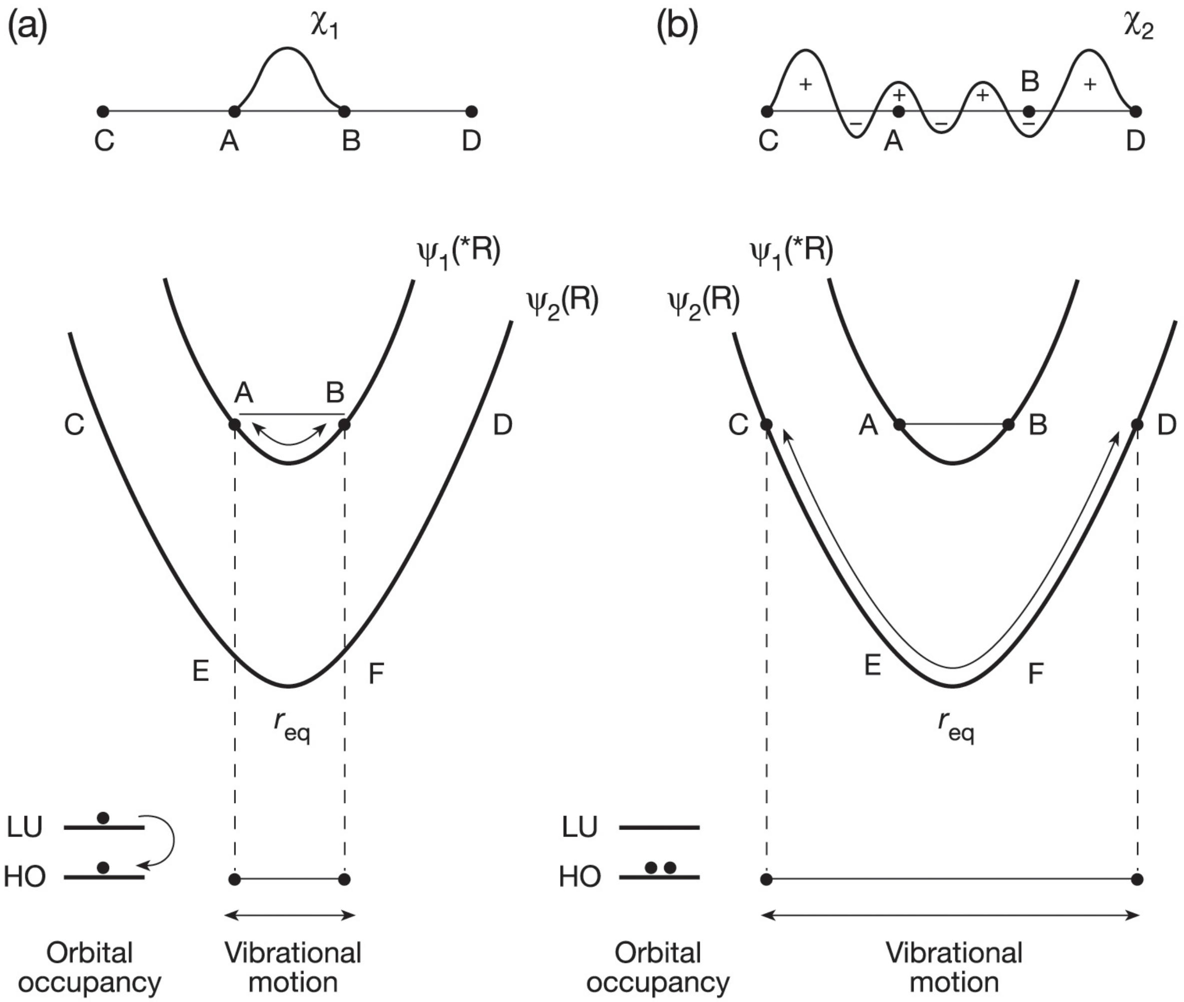
The Franck–Condon Principle for Radiationless Transitions

- In contrast to radiative transitions, *vertical jumps between PE curves separated by a large energy gap are improbable because of the need to conserve energy during a radiationless transition*

- It is easier to conserve energy for radiationless transitions at points for which curves cross or come close together, since at the crossing points the wave functions [e.g., Ψ_1(*R) and Ψ_2(R)] have exactly the same energy

- On the next slide, we will examine a situation where a molecule starts off on an excited PE curve whose wave function is Ψ_1(*R) and undergoes a Lu → HO electronic transition to Ψ_2(R)

The Franck–Condon Principle for Radiationless Transitions



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The Franck–Condon Principle for Radiationless Transitions

- On the left, the molecule begins in the Ψ_1(*R) state, and on the right, the molecule has just been converted into the Ψ_2(R) state

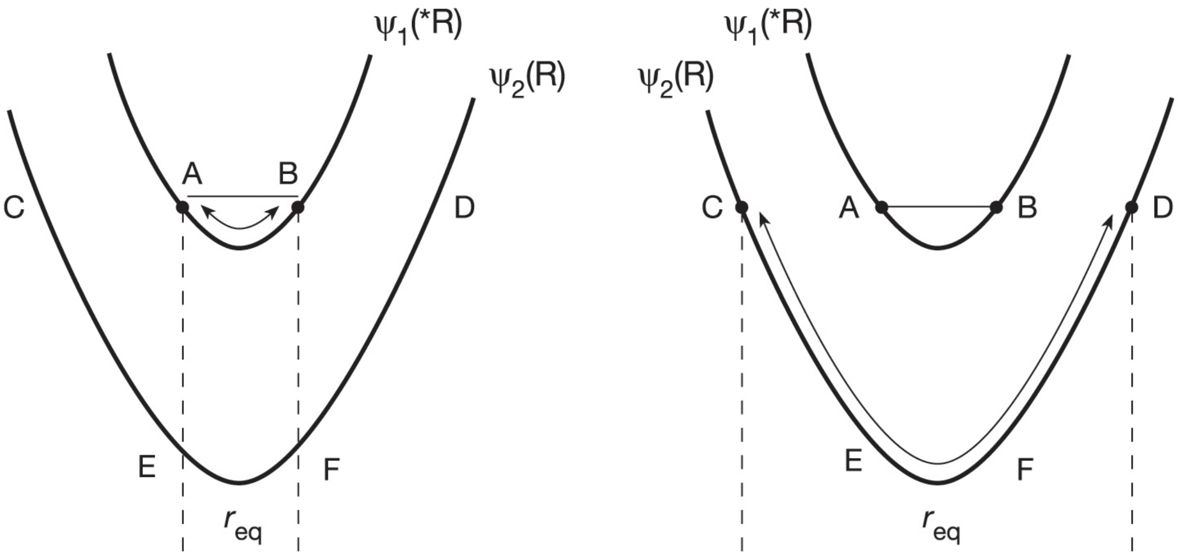
- In Ψ_1(*R), there is a relatively small oscillating trajectory between points A and B on the excited surface [(a)]

- After the transition to Ψ_2(R) [(b)], there is a relatively large oscillation between points C and D because the electronic energy of Ψ_1(*R) has been converted into vibrational energy in Ψ_2(R)

- Remember: For a radiationless transition to be *possible*, energy and momentum must be conserved

The Franck–Condon Principle for Radiationless Transitions

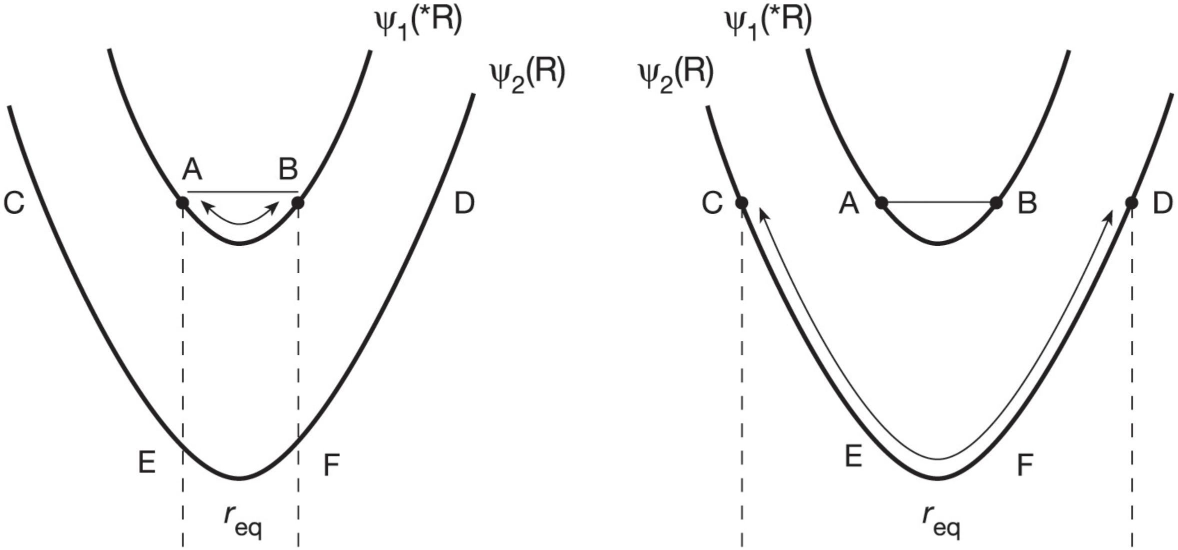
Question: What happens when a *horizontal* jump with conservation of PE (A → C or B → D) occurs, or a *vertical* jump with conservation of geometry (A → E or B → F) occurs?



- A *horizontal* jump from Ψ_1(*R) to Ψ_2(R) that conserves energy requires an unlikely abrupt change in nuclear geometry
- The structures of the initial and final states do not “look alike”, therefore the horizontal jump is improbable

The Franck–Condon Principle for Radiationless Transitions

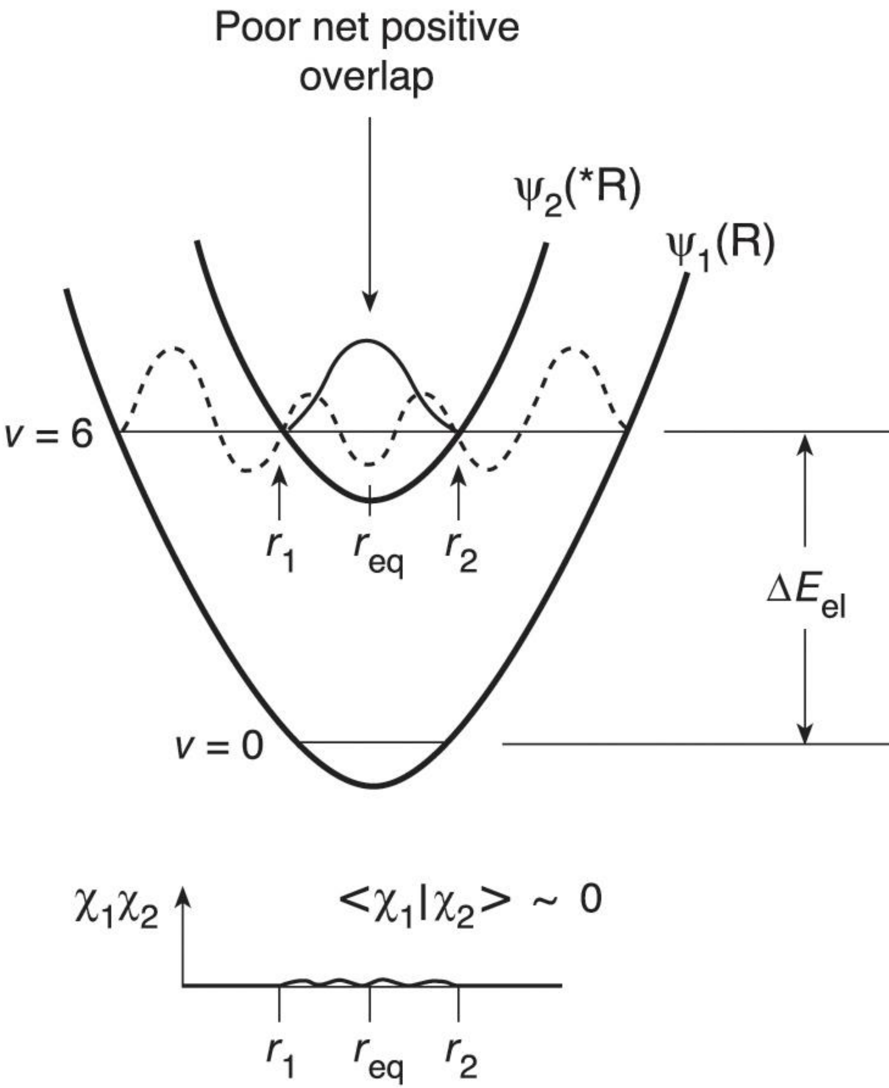
Question: What happens when a *horizontal* jump with conservation of PE (A → C or B → D) occurs, or a *vertical* jump with conservation of geometry (A → E or B → F) occurs?



- A *vertical* jump that conserves initial geometry from Ψ_1(*R) to Ψ_2(R) with result in an abrupt change in the amplitude of vibration
- The energetics of the initial and final states do not “look alike”, therefore the vertical jump is improbable

The Franck–Condon Principle for Radiationless Transitions

- Let’s add the quantum mechanical wave functions for the vibrations for the transition Ψ_1(*R) → Ψ_2(R)
- Suppose the wave functions χ_1 and χ_2 correspond to the $\upsilon = 0$ and $\upsilon = 6$ vibrations of Ψ_1(*R) and Ψ_2(R), respectively
- The vibrational wave functions for initial (χ_1, $\upsilon = 0$) and the final state (χ_2, $\upsilon = 6$) do not look at all alike
- The dissimilarities lead to the conclusion that the overlap integral ($< \chi_1 | \chi_2 >$) will have a value close to 0 (wave functions essentially cancel out)
- Transition implausible and will occur at a slow rate



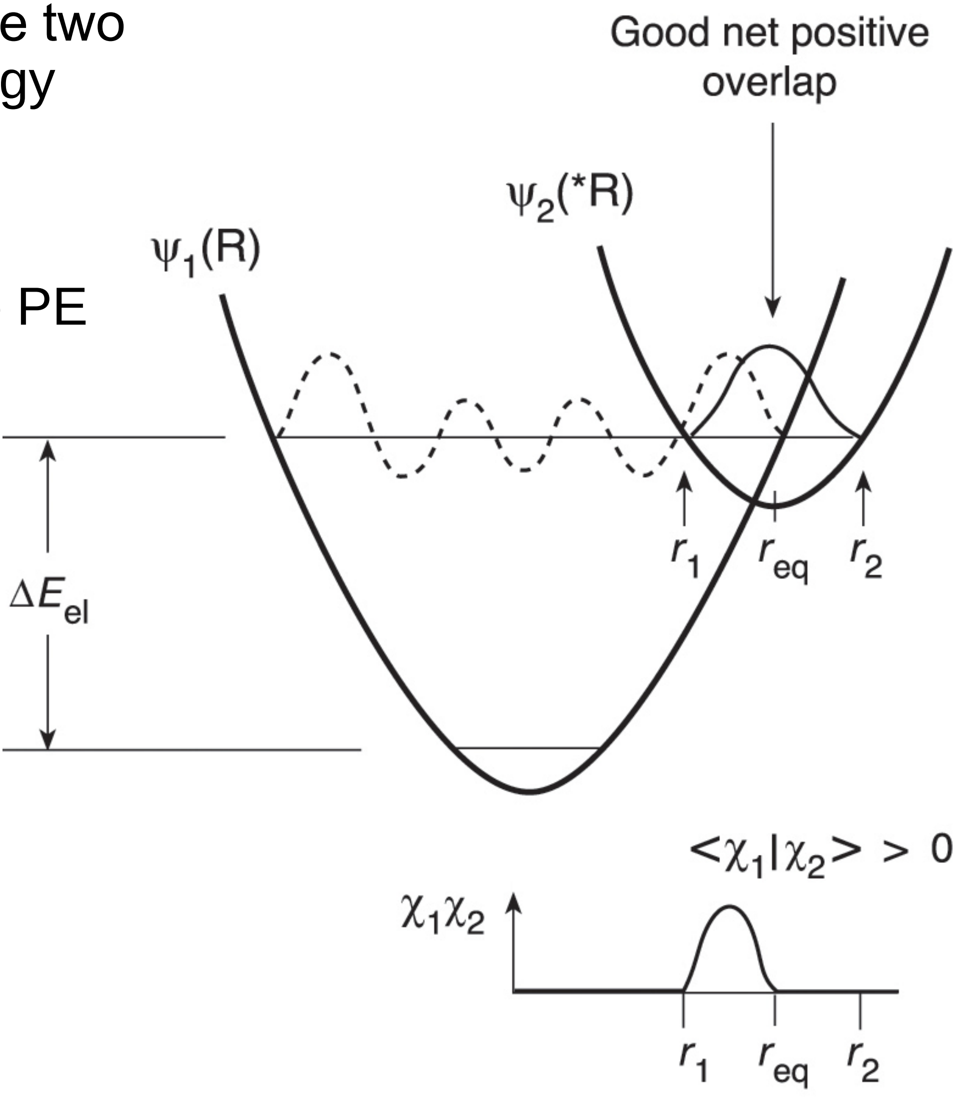
The Franck–Condon Principle for Radiationless Transitions

- Now let’s consider a situation where two PE curves come very close in energy (i.e., they actually intersect)

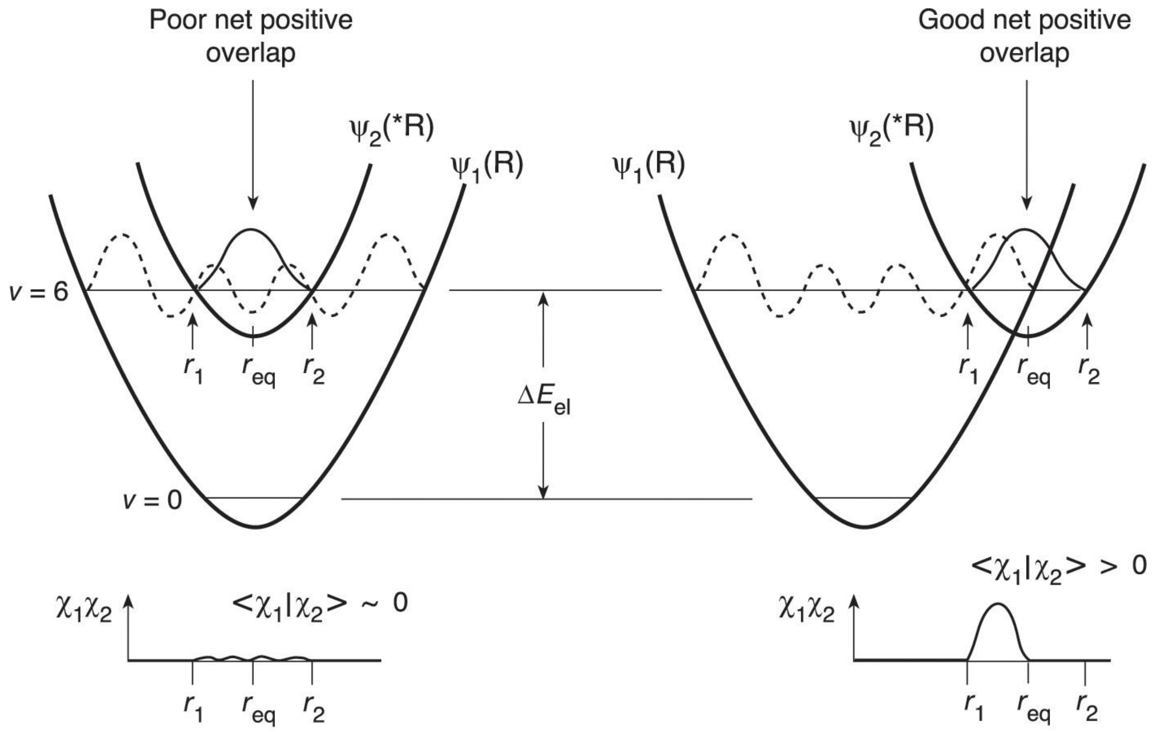
- There is a specific value of *r* where PE curve-crossing occurs

- Significant overlap of the vibrational wave functions χ_1 and χ_2, leading to an overlap integral ($< \chi_1|\chi_2 >$) > 0

- Raditionless transition for this surface-crossing situation is plausible and will occur at a fast rate



The Franck–Condon Principle for Radiationless Transitions



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In terms of a selection rule,

- A radiationless transition when there is no surface crossing (left) is *Franck–Condon forbidden* (i.e. the FC factor $(<\chi_1|\chi_2>)^2 \sim 0$)
- A radiationless transition at the surface-crossing (right) is *Franck–Condon forbidden* (i.e. the FC factor $(<\chi_1|\chi_2>)^2 \neq 0$)

The Franck–Condon Principle for Radiationless Transitions

- In summary, *raditionless transitions are most probable when two PE curves for vibrations cross (or come very close to one another), because when this happens, it is easiest to conserve the energy, motion, and phase of the nuclei during the transition in the region of the crossing*

- In other words, in the regions of curve crossings, the wave functions of R and *R look alike structurally, energetically, and dynamically

Transitions between Spin States of Different Multiplicity

- Some of the most important spin transitions in organic photochemical reactions involve a change in spin, specifically the conversion of a singlet state to a triplet state or vice versa

- Consider the spin wave function for an initial spin state ($\boldsymbol{S}_1$) and a final spin state ($\boldsymbol{S}_2$)

- Analogous to the vibrational overlap integral ($< \chi_1|\chi_2 >$), there is a spin overlap integral ($< \mathcal{S}_1|\mathcal{S}_2 >$)

- When there is no spin change during the transition, ($< \mathcal{S}_1|\mathcal{S}_2 >$) = 1

- Initial and final spin states look alike and there is no spin prohibition on the electronic transition (*spin allowed*)

Transitions between Spin States of Different Multiplicity

- When there is spin change during the transition, $(< \mathcal{S}_1 | \mathcal{S}_2 >) \neq 1$, and the transition is strictly forbidden

- Transitions between singlets and triplets becomes allowed only if an interaction for mixing of spin states is available
  - Requires *magnetic interactions*

- An electronic transition that involves a change of spin angular momentum requires some interaction (coupling) with another source of angular momentum that can both trigger the transition and allow conservation of the total angular momentum and the conservation of *magnetic energy*

- For organic molecules, the most important interaction is the coupling of the electron spin with the orbital angular momentum (i.e. spin–orbit coupling)

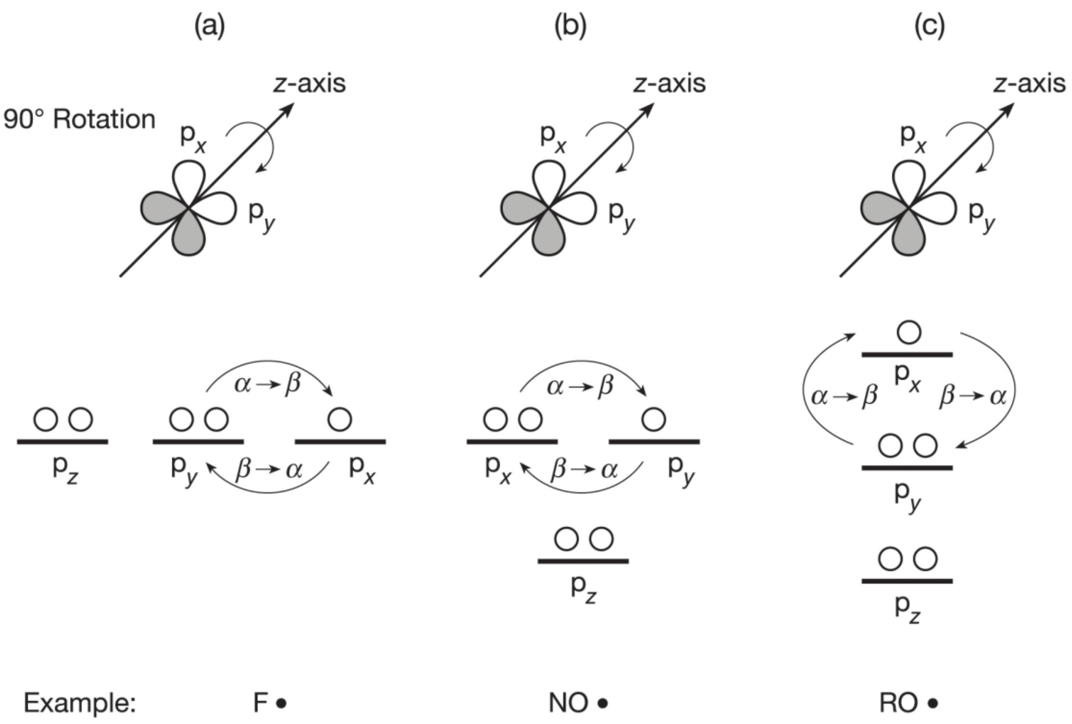
Spin–Orbit Coupling

- Let’s examine the spin–orbit coupling associated with an electron in a p orbital, which is typically the most important atomic orbital for both *R and I(D)

- An electron in a p orbital possesses one unit of angular momentum, exactly the amount of angular momentum required to change an electron’s spin orientation from $\alpha(+1/2) \rightarrow \beta(-1/2)$ or vice-versa

- For angular momentum to be conserved during a change in spin orientation on a unit of angular momentum, the p orbital that is coupled to the electron spin must change its orientation by exactly one unit of angular momentum

Spin–Orbit Coupling



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- The p orbital can produce one unit of angular momentum by undergoing a 90° rotation around an arbitrary z-axis, a move that is equivalent to overlapping with an adjacent p orbital [(a)]
- Rotation is favored when the energy of the p_x and p_y orbitals are identical; when the energies differ, the electrons become trapped in a p orbital of lower energy [(c)]
  - Rotation is inhibited or angular momentum of the electron is “quenched”

Spin–Orbit Coupling

- For examples (a) and (b), the $p_x \rightarrow p_y$ jump can occur between orbitals of exactly the same energy, but for (c), the $p_x \rightarrow p_y$ jump must occur between orbitals of different energy
- The mixing of states is much stronger for states with similar or identical energies than the mixing of states with different energies
- The mixing of spin states corresponds to the generation of orbital angular momentum due to a $p_x \rightarrow p_y$ jump
- We can visualize the circular orbital motion "twisting" about an axis, which is the essence of the generation of angular momentum
- The larger the orbital angular momentum generated, the larger the magnetic moment generated by orbital motion, and the stronger the spin–orbit coupling

- The closer the system is to examples (a) and (b), the stronger the spin–orbit coupling, and the faster the rate of intersystem crossing (ISC)

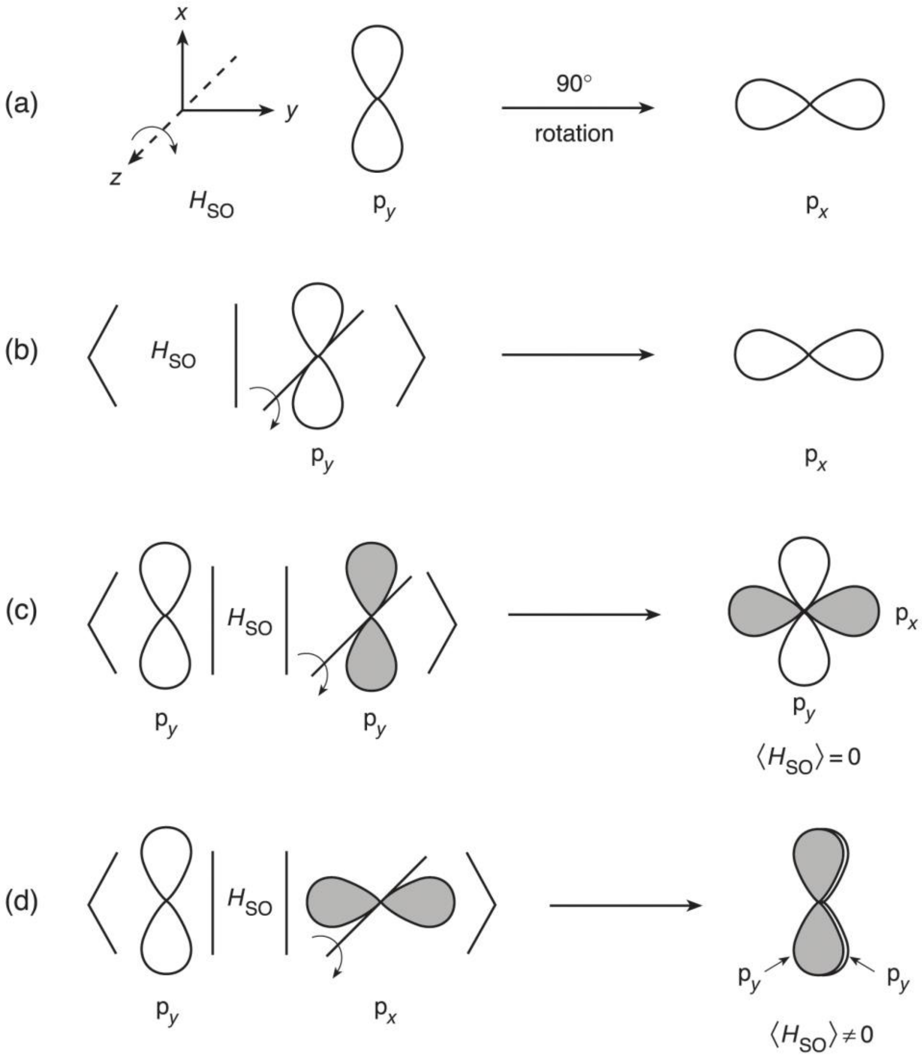
Spin–Orbit Coupling

- When *R possesses an electronic distribution for which there is significant contribution of a half-filled orbital on a single-atom (e.g., the situation for the n orbital of an n,π* state), strong spin–orbit coupling is *plausible*

- If *R *does not* possess an electronic distribution for which there is significant contribution of half-filled orbitals on a single-atom (e.g., the situation for π,π* states), strong spin–orbit coupling is implausible

Spin–Orbit Coupling

- The orientation of the p_x and p_y orbitals relative to the x-, y-, and z-axis are shown in (a)
- The strength of the spin–orbit coupling depends on the net overlap between the orbitals, in other words, the magnitude of spin–orbit coupling is proportional to the overlap integral
- If two p_y orbitals are involed (c), the orbital overlap on the same atom is given by $\left(< \mathrm{p}_x | \mathrm{p}_y > = 0\right)$, therefore the magnitude of the spin–orbit coupling will be 0!



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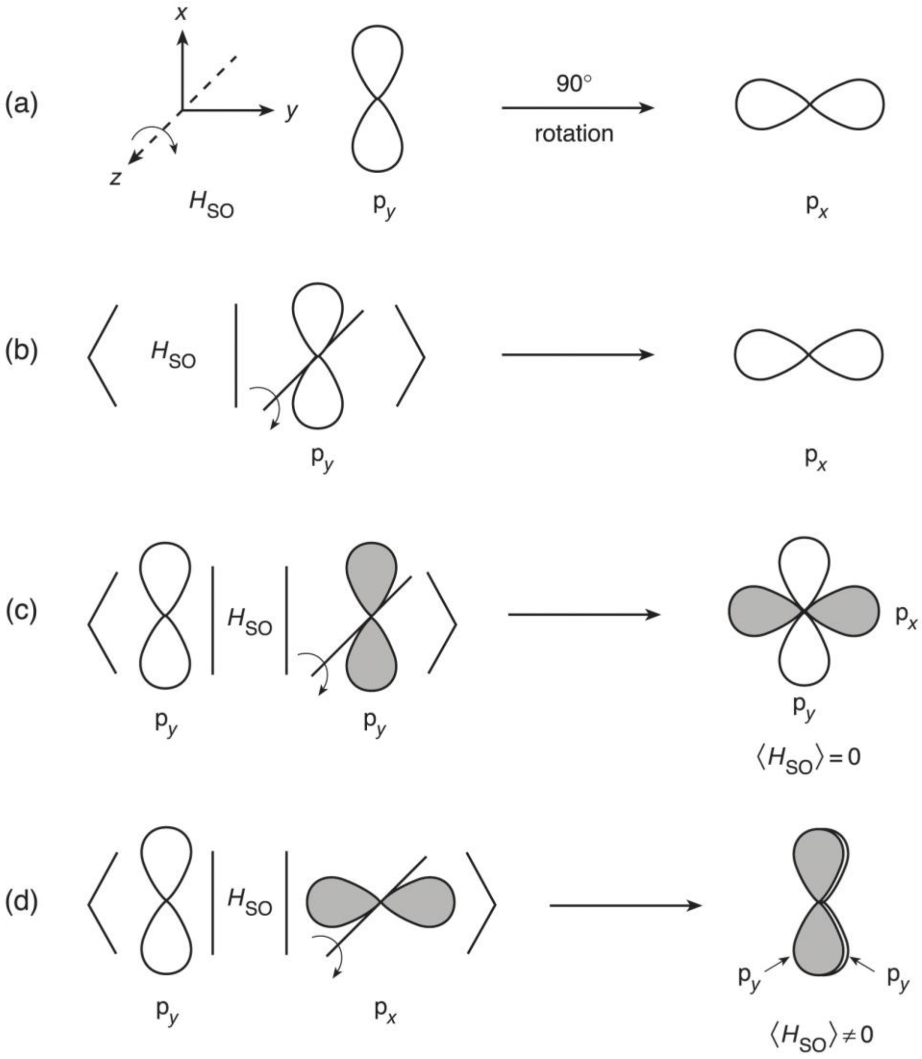
Spin–Orbit Coupling

- The orientation of the p_x and p_y orbitals relative to the x-, y-, and z-axis are shown in (a)
- The strength of the spin–orbit coupling depends on the net overlap between the orbitals, in other words, the magnitude of spin–orbit coupling is proportional to the overlap integral
- If a p_x and p_y orbital are involved, rotating p_x by 90° converts it into a p orbital
- There is a good overlap $(< \mathrm{p}_y | \mathrm{p}_y >)$ and strong spin–orbit coupling!



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Spin–Orbit Coupling

- Spin–orbit coupling constant, ζ_{SO}: related to the nuclear charge the electron "sees" as it orbits its key atoms involved in the intersystem crossing step

- The magnitude of the spin–orbit coupling constant ζ_{SO} for organic molecules containing only "light" atoms (e.g., H, C, O, N, and F) is typically much smaller (~ 0.01 – 0.1 kcal mol^{-1}) than vibrational energies (~ 0.5 – 5 kcal mol^{-1}) , but the magnitude of ζ_{SO} for "heavy atoms (e.g., Br or Pd) can be large and can even exceed the values of vibrational energy

- For atoms, the dependence of spin–orbit coupling is directly proportional to the nuclear charge, Z

- *The higher the Z value, the greater the acceleration as the electron approaches the nucleus, and the greater the extent of spin–orbit coupling*
  - Creates a strong magnetic moment as the result of orbital motion

Spin–Orbit Coupling

We can now deduce the following selection rules for effective spin–orbit coupling:

Rule 1:

The orbitals involved in the $p_x \rightarrow p_y$ transition must be similar in energy. For a large energy difference between these orbitals, orbital angular momentum and therefore spin-orbital coupling through angular momentum is “quenched”

Spin–Orbit Coupling

We can now deduce the following selection rules for effective spin–orbit coupling:

Rule 2:

Spin–orbit coupling in organic molecules will be effective in inducing transitions between different spin states if a “$p_x \rightarrow p_y$” orbital transition if a single atom is involved because such an orbital transition provides a means of conserving total angular momentum as well as means of generating angular momentum

Spin–Orbit Coupling

We can now deduce the following selection rules for effective spin–orbit coupling:

Rule 3:

Spin–orbit coupling in organic molecules will be effective in inducing transitions between different spin states if one (or both) of the electrons involved approaches a “heavy” atom nucleus causing the electron to accelerate and thereby create a strong magnetic moment as the result of orbital motion

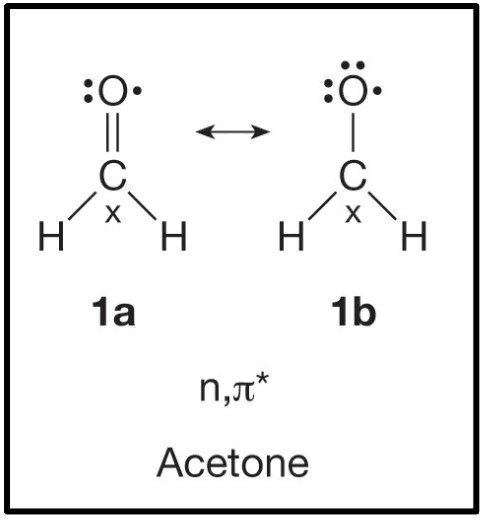
Spin–Orbit Coupling

- Some representative values of ζ_{SO} are listed in the Table below
- For spin–orbit coupling considerations, elements from $Z = 1$ (hydrogen) to $Z = 10$ (neon) are considered to be “light” atoms and elements with $Z > 10$ are considered to be “heavy” atoms

Element	**Atomic Number (Z)**	**ζ_{SO} (kcal mol^{-1})**
H	1	< 0.1
C	6	0.1
N	7	0.2
O	8	0.4
F	9	0.8
Cl	17	2
Br	35	7
I	53	14

Spin–Orbit Coupling

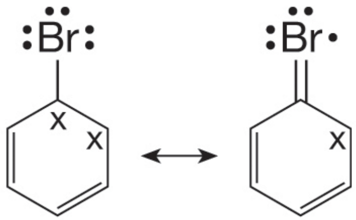
- Let’s discuss the spin–orbit coupling for the n,π* state of acetone
- We have previously seen that a transition between p orbitals provides one of the best mechanisms for coupling spin and angular momentum
- In the case of acetone, there are two resonance structures that approximate the n,π* state



- The single dot (•) represents an electron in the p orbital on the oxygen atom and the single “x” represents an electron in an antibonding orbital
- The odd electron on the oxygen atom has an available $p_x \rightarrow p_y$ transition that can serve to induce spin–orbit coupling

Spin–Orbit Coupling

- Let’s discuss the spin–orbit coupling for the π,π^* state of bromobenzene
- Structure **2a** corresponds to the π,π^* state with excitation on the benzene group (“x” represents a π or π^* electron) and **2b** corresponds to the π,π^* state with excitation on the Br atom



2a **2b**

π,π^*

Bromobenzene

- To the extent that structure **2b** contributes to the π,π^*, there will be a certain probability that one of the electrons in a half-filled orbital will be located for a period of time on the Br atom
- During this time, the electron will both experience the strong positive charge from the nucleus (Z = 35) and have an opportunity to undergo a $p_x \rightarrow p_y$ orbital jump, both of which favor spin–orbit coupling

Up Next…

Chapter 4: Radiative Transitions between Electronic States