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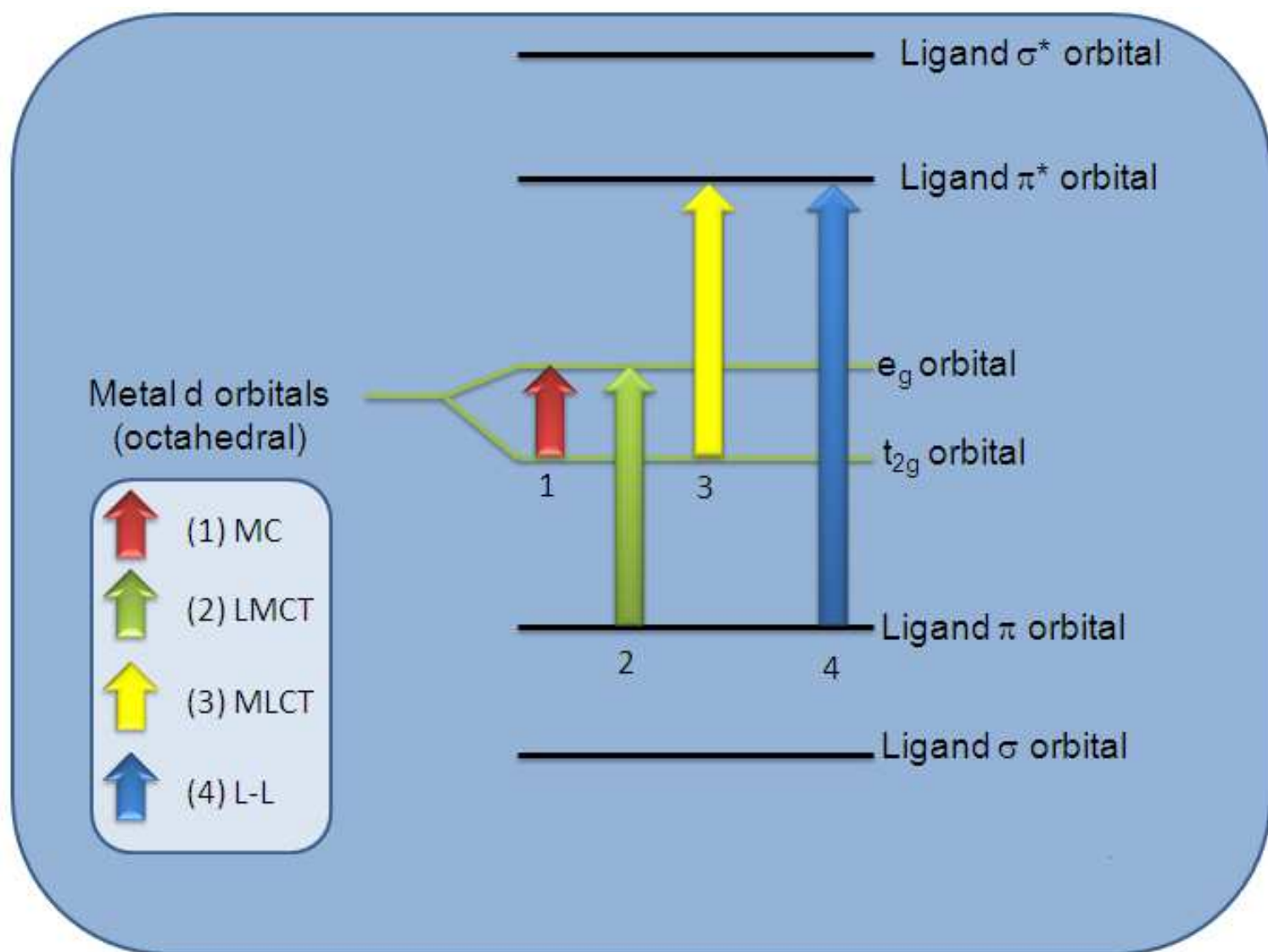
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Electronic Properties of d_π^6 Coordination Compounds

The metal-to-ligand charge transfer (MLCT) excited states of d_π^6 coordination compounds have emerged as the most efficient for both solar cells and Organic Light-Emitting Diodes.

The focus will be on the redox potentials and absorption and emission spectra of $M(L)_6^{2+}$ compounds ($M = \text{Fe(II)}, \text{Ru(II)}, \text{and Os(II)}$), as well as Ir(III) complexes, where L includes various ligands.

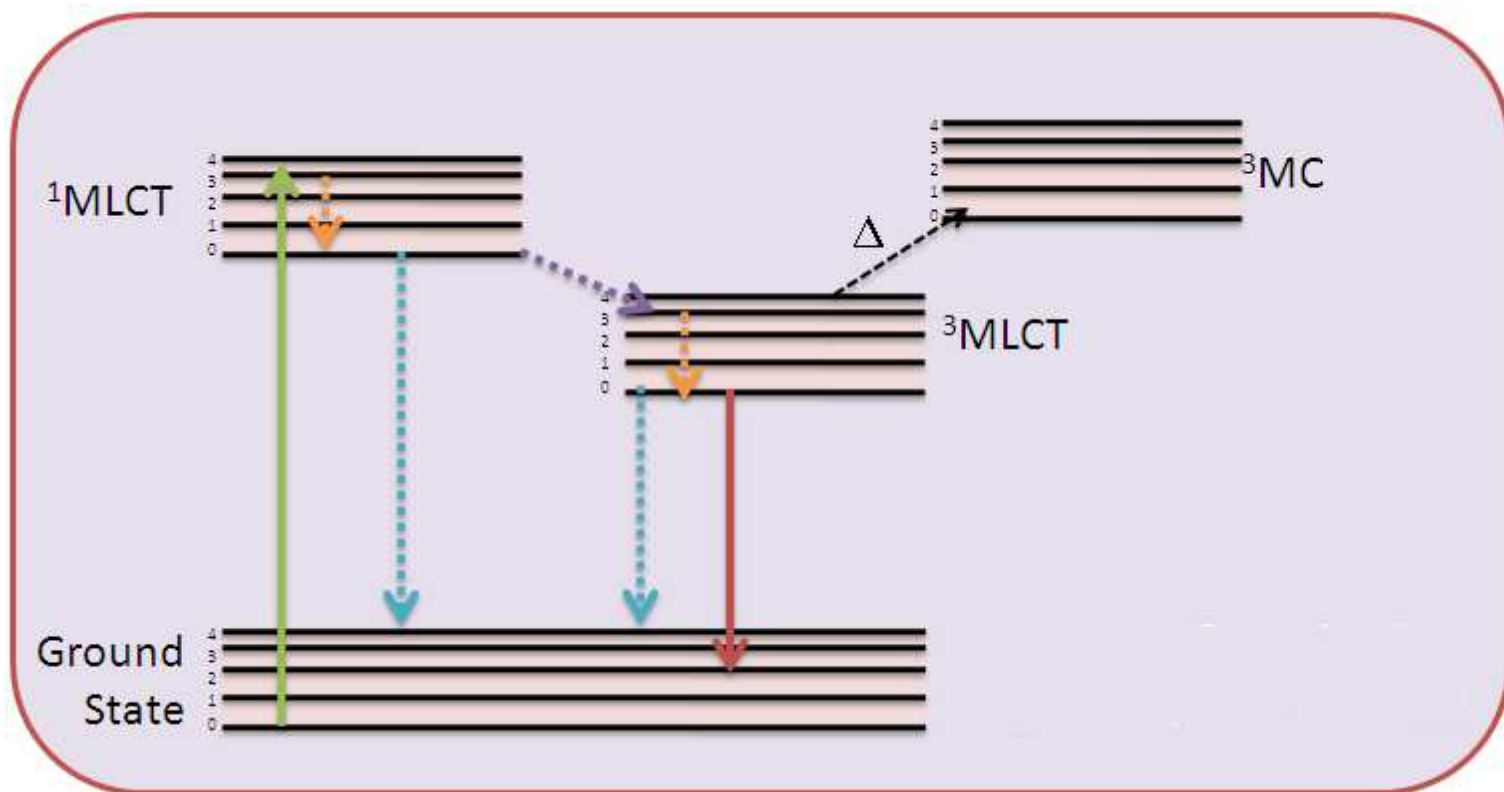
Light absorption transitions in octahedral complexes: metal centered (MC); ligand-to-metal charge transfer (LMCT); metal-to-ligand charge transfer (MLCT); and ligand-ligand (L-L)





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Jablonski diagram for a $\text{Ru}(\text{bpy})_3^{2+}$ complex. Solid lines indicate a radiative process while dashed lines indicate a non-radiative process.

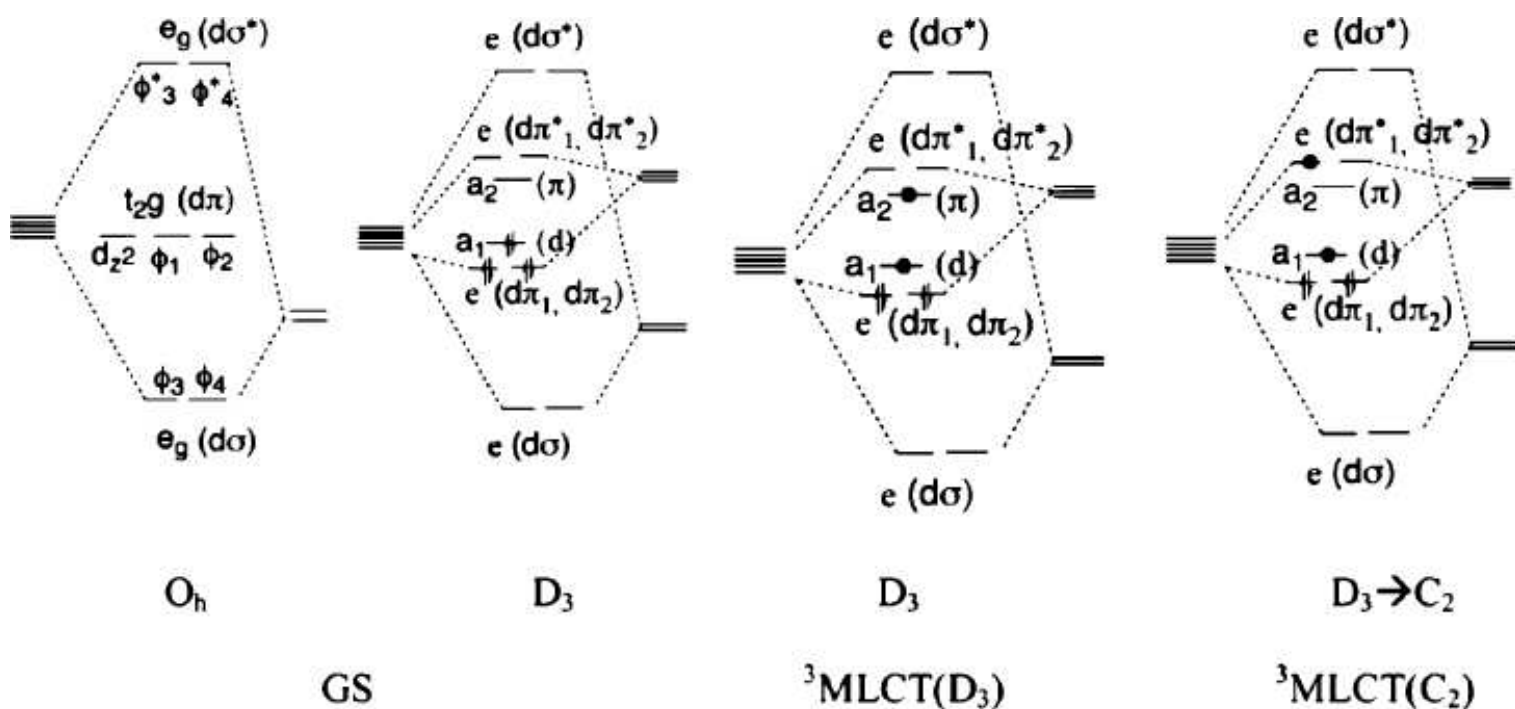
The effects of spin-orbit coupling must be introduced to explain the relative oscillator strengths and absorption spectra of these complexes.



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Molecular Orbital Diagram for $\text{Ru}(\text{L})_6^{2+}$ Complexes In Their Ground State

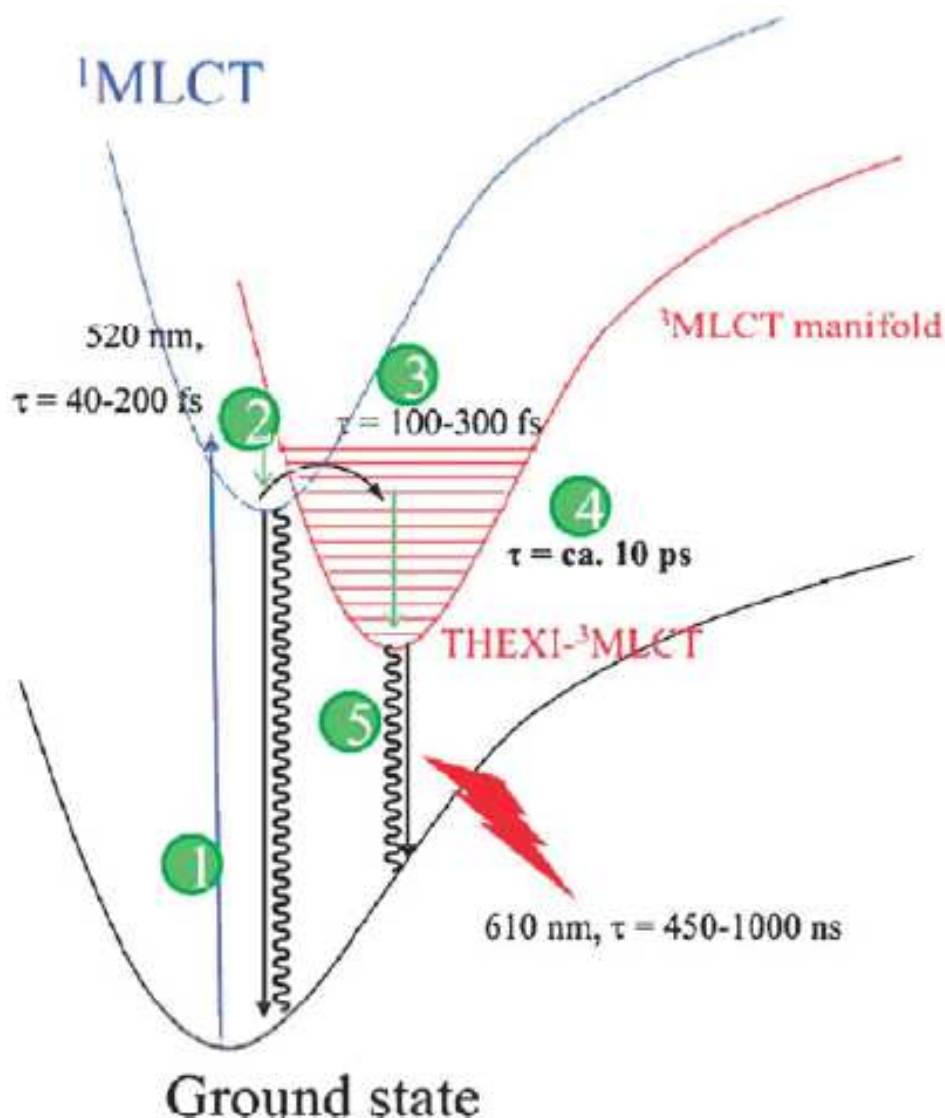




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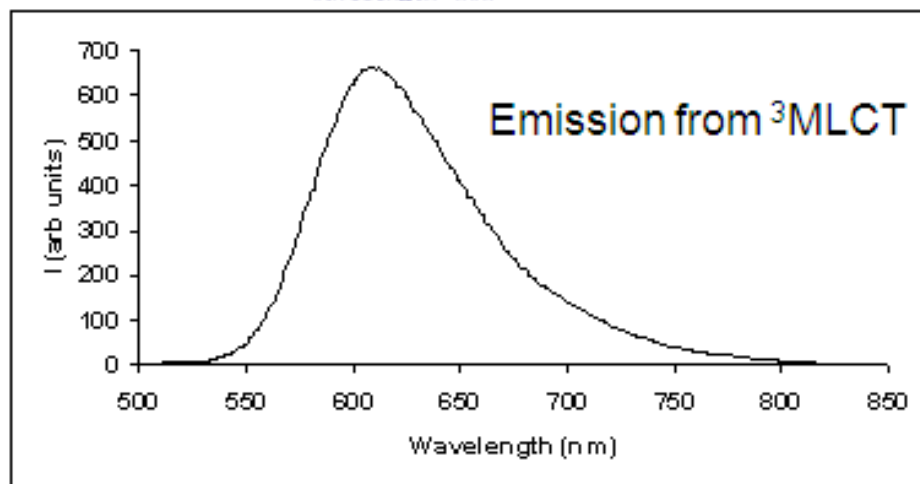
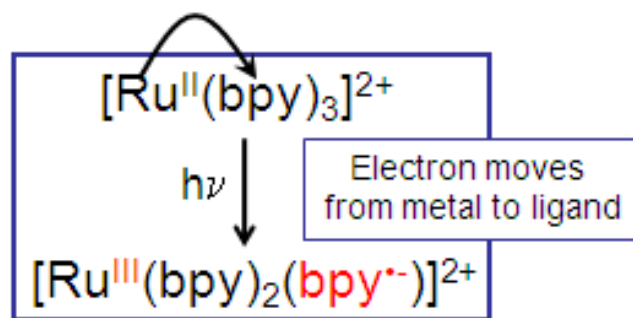
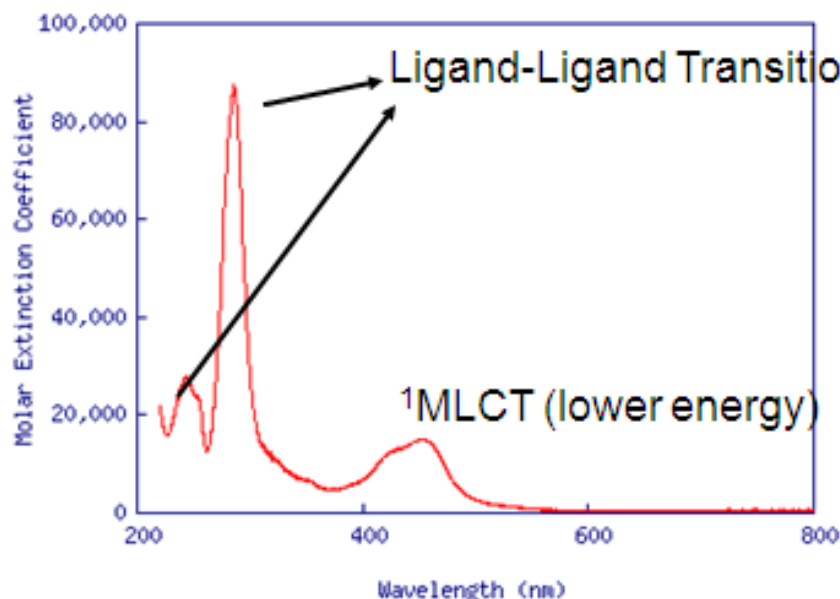
Potential energy surfaces illustrating the relative electronic and vibrational lifetimes for $\text{Ru}(\text{bpy})_3^{2+}$. Both internal conversion thermal relaxation(2) and intersystem crossing(3) occur in the sub-picosecond time scale while the life-time of the *thexi* state(5) is up to a microsecond.





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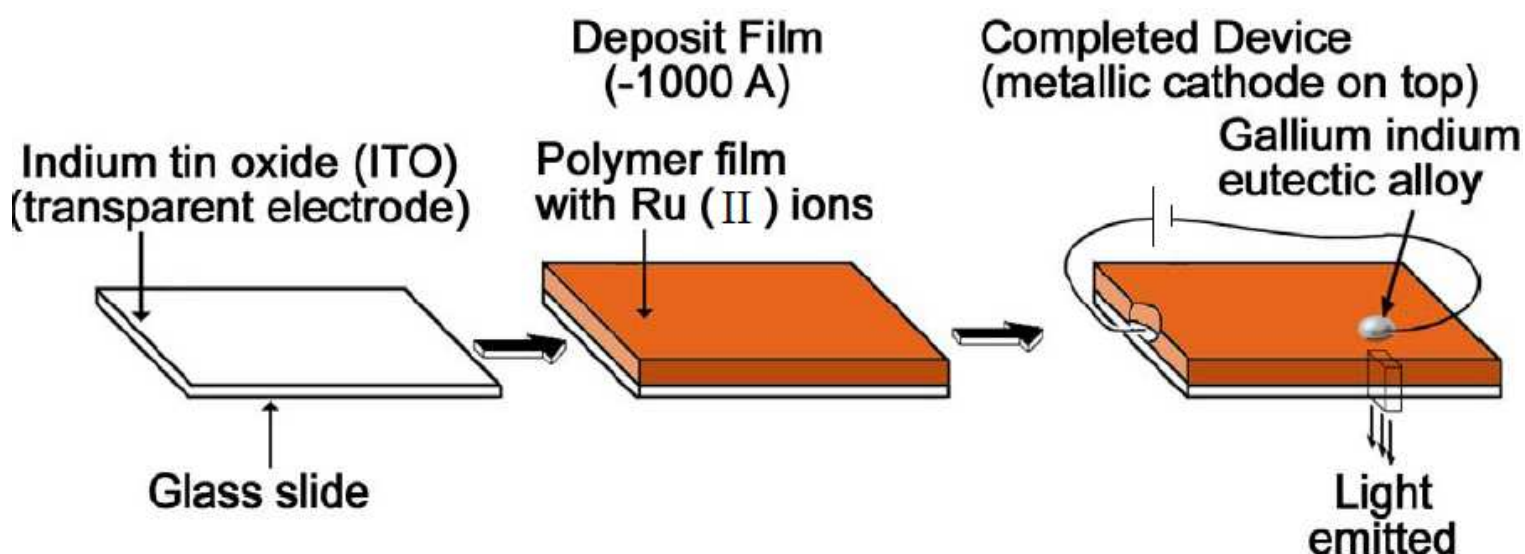
Absorption spectrum (top) and emission spectrum (bottom) for $\text{Ru}(\text{bpy})_3^{2+}$ in water. Ruthenium absorbs at 450 nm (2.8 eV) and emits strongly at ≈ 620 nm (≈ 2.0 eV) in water which is caused by a radiative process from the ³MLCT state to the ground state.



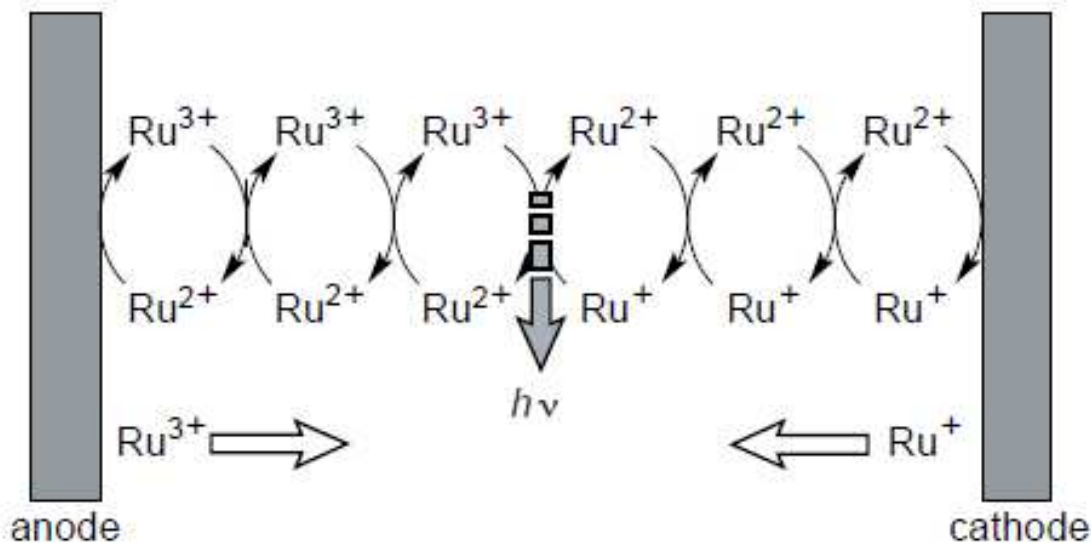
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Organic Light-Emitting Diodes



Electron Transfer Through the Ruthenium film Showing Oxidation Occurring at the Anode and Reduction Occurring at the Cathode





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A Working OLED

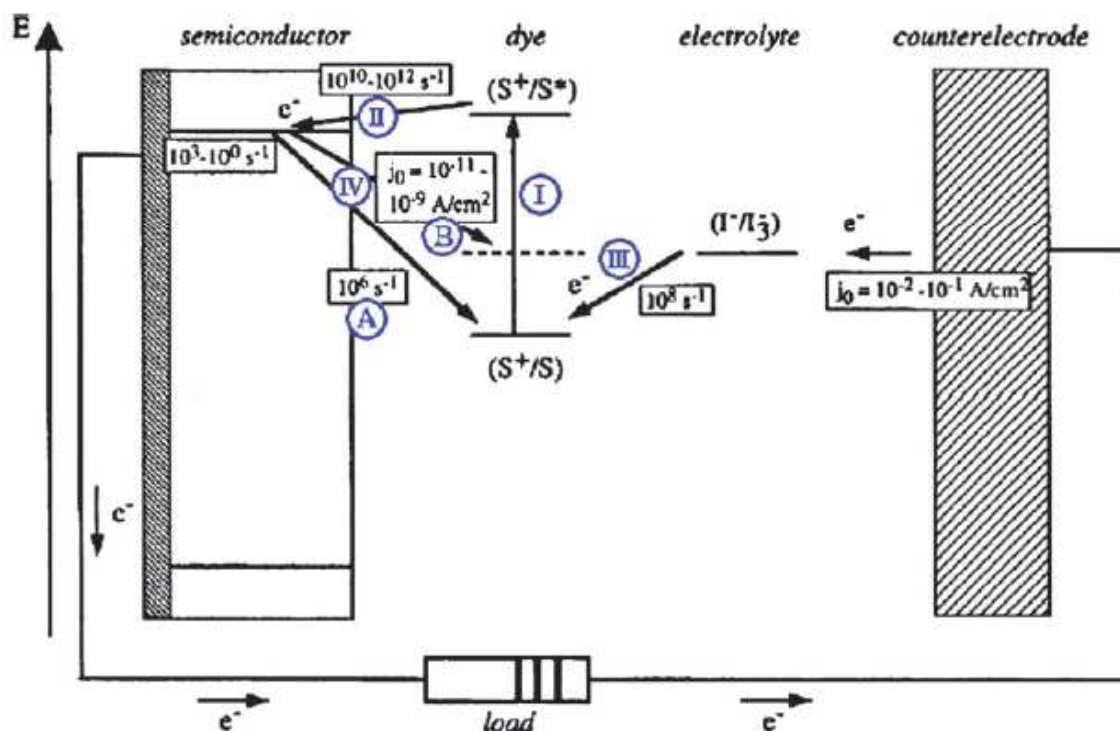




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Schematic Diagram Depicting a Dye-Sensitive Solar Cell (DSSC)



- I** Light is absorbed by a sensitizer to form a molecular excited state.
- II** The excited state may eject an electron into the semiconductor, thus causing charge separation.
- III** The oxidized sensitizer is regenerated by an external electron donor.
- IV** The unwanted charge recombination of TiO_2 electrons goes to **A**, oxidized sensitizers or **B**, oxidized donors in the electrolyte.



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d-Orbital Splitting Diagrams

First-row transition metals may be either low spin or high spin.

Because tetrahedral complexes have much smaller d-orbital splitting (Δ_t) than octahedral complexes (Δ_o), almost all tetrahedral first-row transition metal complexes are high spin.

For octahedral complexes, the nature of the ligand plays a major role in determining whether the complex is low spin or high spin. Weak-field ligands give rise to small Δ_o and thus are high spin. Strong-field ligands give rise to large Δ_o and are low spin.

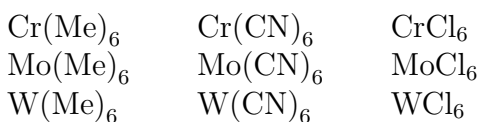
As one moves down a transition metal group, the d-orbital splitting, Δ_o increases. For this reason, almost all second- and third-row transition metal complexes are low spin.

Assignment (Ligand Field Splitting)

In this part of Project IV, the d-orbital splitting diagrams for a series of transition molecules are investigated, and the values of Δ_o are compared with different types of ligand donors and acceptors (pure σ -donors versus π -acceptors versus π -donors) and different transition metals (1st row versus 2nd row versus 3rd row).

1. Perform calculations at fixed geometries for each molecule below, and determine the corresponding value of Δ_o .

The M-C bond distances are fixed at 2.1 Å in both $M(\text{Me})_6$ and $M(\text{CN})_6$ molecules while the M-Cl distances are all kept fixed at 2.30 Å. No optimization is performed, and the results are obtained from single-point calculations.



2. How does the Δ_o splitting vary between 1st row and 2nd row transition metals? What factors lead to this difference? Is a similar difference observed when comparing 2nd row versus 3rd row transition metals? Why or why not?
3. How do the different monoanionic ligands effect the value of Δ_o when the metal is held constant? What is the inherent difference among these three ligands?
4. Use pictorial representations of the molecular orbitals in interaction diagrams to illustrate your answer to Question #3.

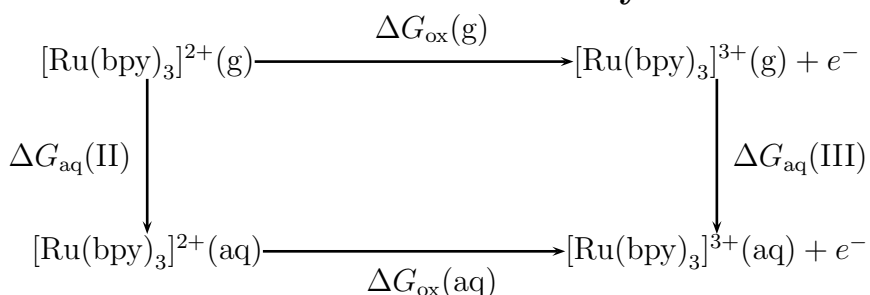


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Redox Potentials for Transition Metal Complexes Used for DSSCs

Ab Initio Redox Potentials: the Born-Haber Cycle



The redox potential ($E_m^{(2+/3+)}$) is obtained from

$$\Delta G(\text{aq}) = -n F E_m^{(2+/3+)}$$

where $n = 1$, i.e. the number of electrons involved in the redox process, $F = 96,500 \text{ C}$,

$$\Delta G_{\text{ox}}(\text{aq}) = \Delta G_{\text{ox}}(\text{g}) + \Delta G_{\text{aq}}(\text{III}) - \Delta G_{\text{aq}}(\text{II})$$

and

$$\Delta G_{\text{ox}}(\text{g}) = G[\text{Ru}(\text{bpy})_3^{3+}(\text{g})] - G[\text{Ru}(\text{bpy})_3^{2+}(\text{g})]$$

with $G^0 = H^0 - TS^0$ where H^0 is the molecular enthalpy obtained from the minimum energy structure, and S^0 is the molecular entropy obtained from a frequency calculation.



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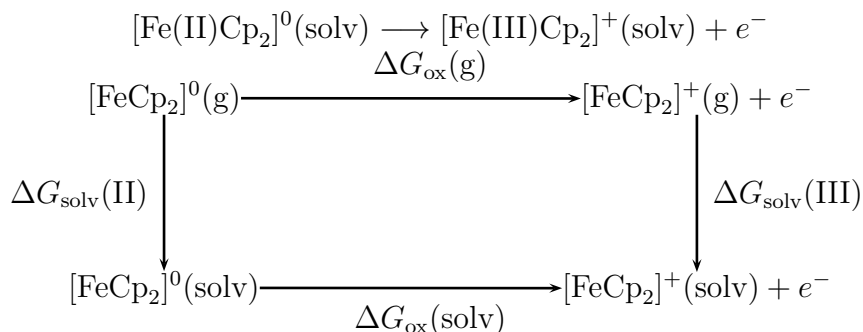
Redox Potentials for Transition Metal Complexes Used for DSSCs

Example Calculation: Redox Potential for $[\text{FeCp}_2]^{0/+}$

As an example of how to do this part of the assignment, we will compute the redox potential

$$\Delta G(\text{aq}) = -n F E_m^{(0/+)}$$

from a calculation for the Gibbs free energy change, $\Delta G_{\text{ox}}(\text{sol})$, for the reaction



Using the Born-Haber Cycle, we obtain:

$$\Delta G_{\text{ox}}(\text{solv}) = \Delta G_{\text{ox}}(\text{g}) + \Delta G_{\text{solv}}(\text{III}) - \Delta G_{\text{solv}}(\text{II})$$

where

$$\Delta G_{\text{solv}}(\text{II}) = E_{\text{solv}}^{\text{scf}}(\text{II}) - E_{\text{g}}^{\text{scf}}(\text{II})$$

$$\Delta G_{\text{solv}}(\text{III}) = E_{\text{solv}}^{\text{scf}}(\text{III}) - E_{\text{g}}^{\text{scf}}(\text{III})$$

$$\Delta G_{\text{ox}}(\text{g}) = (E_{\text{g}}^{\text{scf}}(\text{III}) + \text{Gibbs Correction}(\text{g}, \text{III})) - (E_{\text{g}}^{\text{scf}}(\text{II}) + \text{Gibbs Correction}(\text{g}, \text{II}))$$



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Redox Potentials for Transition Metal Complexes Used for DSSCs

Example Calculation: Redox Potential for $[\text{FeCp}_2]^{0/+}$

Tabulated Energies (au) from Calculations			
$[\text{FeCp}_2]^0$		$[\text{FeCp}_2]^+$	
$E_g^{\text{scf}}(\text{II})$	-510.439067386	$E_g^{\text{scf}}(\text{III})$	-510.170289413
Gibbs Correction (g, II)	0.134232	Gibbs Correction (g, III)	0.132483
$E_{\text{solv}}^{\text{scf}}(\text{II})$	-510.444248948	$E_{\text{solv}}^{\text{scf}}(\text{III})$	-510.239713457

Calculated Free Energy Values (au)	
$\Delta G_{\text{solv}}(\text{II})$	-0.005181562
$\Delta G_{\text{solv}}(\text{III})$	-0.069424027
$\Delta G_{\text{ox}}(\text{g})$	+0.267028973
$\Delta G_{\text{ox}}(\text{solv})$	+0.202786508

$$E_m^{0/+} = - \frac{(-0.202786508 \text{ au}) \times 627.51 \text{ kcal/mol}}{(1) \times 96500 \text{ C/mol}} \times \frac{4186 \text{ J}}{\text{kcal}} \times \frac{1 \text{ V}}{\text{J/C}} \approx 5.52 \text{ V}$$

Experimental Determination of $E_m^{0/+}$ for $[\text{FeCp}_2]^0$

Experimental Determination of $E_m^{0/+}$	
E^0 (Absolute Reduction Potential, NHE)	4.60 V
E^0 (Saturated Calomel Electrode (SCE), Relative to NHE)	0.26 V
$E_m^{0/+}$ (Relative to SCE)	0.43 V
$E_m^{0/+}$ (Relative to NHE)	5.29 V

Notes on Comparing Calculated and Experimental Redox Potentials

- Experimental redox potentials are reported relative to a standard electrode.
- If the standard is the **Normal Hydrogen Electrode (NHE)**, then 4.6 V is either subtracted from the absolute reduction potential (i.e. the cost of free electron) or added to the absolute oxidation potential (return of remove electron) in order to determine the potential.
- Adjustment to other standard electrodes is straightforward, since their potentials relative to the NHE is known.



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Redox Potentials for Transition Metal Complexes Used for DSSCs

Assignment (Redox Potentials of DSSCs)

Consider the redox pairs $[\text{MCp}_2]^{0/+}$, and $[\text{MCp}_2^*]^{0/+}$ where $\text{M} = \text{Fe}, \text{Co}$, and $\text{Cp} = \eta - \text{C}_5\text{H}_5$, $\text{Cp}^* = \eta - \text{C}_5\text{Me}_5$.

1. Obtain minimum energy structures for $[\text{CoCp}_2]^{0/+}$, $[\text{FeCp}_2]^{0/+}$, and $[\text{FeCp}_2^*]^{0/+}$, and compare them to the corresponding X-ray crystal structures.
2. Calculate the redox potential for the $[\text{FeCp}_2]^{0/+}$ pair in acetonitrile ($\text{CH}_3\text{-C}\equiv\text{N}$) which will act as the standard electrode for Question #3.
3. Calculate the redox potentials for the $[\text{FeCp}_2^*]^{0/+}$ and $[\text{CoCp}_2]^{0/+}$ pairs in acetonitrile ($\text{CH}_3\text{-C}\equiv\text{N}$) relative to redox potential obtained for $[\text{FeCp}_2]^{0/+}$ in Question #2.

Compare your results to the experimental values given in Connelly, N.G.; Geiger, W.E., *Chemical Reviews*. **1996**, **96**, 877-910.

4. Construct an orbital interaction diagram for FeCp_2 , and then use this to rationalize all the results obtained from Questions #1, #2, and #3.



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Excited States in Transition Metal Complexes Used for DSSCs

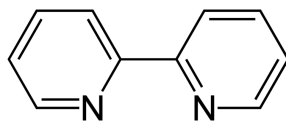
The metal-to-ligand charge transfer (MLCT) excited states of d^6_π coordination compounds have emerged as the most efficient for solar harvesting and sensitization of wide-bandgap semiconductor materials.

Light absorption promotes an electron from the metal d orbitals to the Ligand π^* orbitals, $d_\pi - \pi^*$

A number of electric-dipole-allowed charge-transfer transitions are observed which give rise to intense absorption bands in the visible region with moderate extinction coefficients.

There is no formal spin for each excited state due to heavy-atom spinorbit coupling from the transition-metal center, especially for 4d and 5d metals.

The effects of spin-orbit coupling must be introduced in order to rationalize the relative oscillator strengths and absorption spectra of $[M(\text{bpy})_3]^{2+}$ complexes, where M = Fe(II), Ru(II) and Os(II) transition metals, and bpy is the 2,2'-bipyridine ligand



bpy

The excited-state lifetime of $[\text{Ru(III)}(\text{bpy})_2(\text{bpy})^-]^{2+}$ is $\approx 1 \mu\text{s}$ in water. The radiative rate constant is typically about two orders-of-magnitude smaller than the non-radiative rate constant and hence the excited-state lifetime is controlled by the latter.

Ru(II)- and Os(II)-polypyridyl excited states have been shown to follow the **Energy Gap Law**, where the non-radiative rate constant increases exponentially with decreasing energy gap.

For this reason, it has proven to be difficult to prepare compounds that emit in the infrared region and have long-lived excited states.

A large ligand-field splitting parameter is required for the observation of long lifetimes in this class of excited states. The presence of low-lying, ligand-field states can rapidly deactivate MLCT excited states and decrease excited-state lifetimes.



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TM Complexes Used in Organic Light-Emitting Diodes

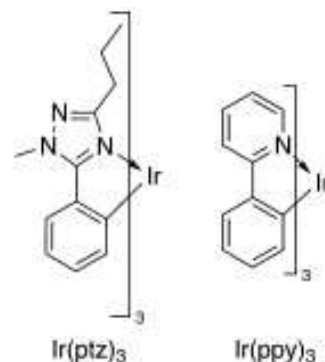
Phosphorescent iridium(III) complexes are showing significant progress as an important component in devices constructed with organic light-emitting diodes (OLEDs).

Phosphorescent materials are much more desirable than fluorescent emitters because it is possible to harvest the triplet-generated excitations in a device.

This field was established with the discovery of the **green** phosphorescent complex, *fac*-tris(2-phenylpyridyl)iridium(III) ($\text{Ir}(\text{ppy})_3$).

However, the transition metal complex, *fac*-tris(1-methyl-5-phenyl-3-*n*-[1,2,4]triazoyl)iridium(III) ($\text{Ir}(\text{ptz})_3$) emits **blue** light.

Both these complexes are shown in the adjacent figure.



Selected properties of $\text{Ir}(\text{ppy})_3$ and $\text{Ir}(\text{ptz})_3$, including photoluminescence quantum yield (PLQY) and emission lifetime are given in the table below:

Complex	PLQY	Lifetime (μs)
$\text{Ir}(\text{ptz})_3$	~ 66	1.08
$\text{Ir}(\text{ppy})_3$	~ 90	1.6

There is motivation to study both these complexes in order to develop an understanding of the differences of these compounds which would lead to an enhanced knowledge of how to design new complexes for OLED applications.



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Excited States in Transition Metal Complexes Used for DSSCs and Organic Light-Emitting Diodes

1. Calculate the low-lying triplet and singlet excited states of $M(\text{bpy})_3^{2+}$ ($M = \text{Fe}, \text{Ru}, \text{and Os}$).
Optimize the ground state in the gas phase, and calculate excited states in the gas phase, water, and acetonitrile at the optimized geometry.
2. Characterize the electronic transitions in terms of a molecular orbital diagram.
Discuss which transitions are allowed by symmetry and dipole polarization. How would changes in solvent polarity effect intensities of absorption and emission bands.
Compare your calculated results and experimental results in terms of solvent shifts.
3. Characterize the molecular orbitals that are active in yielding the low-lying excited states with respect to the mixture of MLCT and LC components.

Below is an example of a table that can be constructed in reporting results on excited states.

$\lambda(\text{nm})$		f		$\psi_i \rightarrow \psi_j$	Character of Excitation	Assignment of Excitation
State	Exptl	Calcd	Calcd	TDDFT		
T ₁	489	490		0.58 (125 \rightarrow 126) - 0.29 (125 \rightarrow 128)	MLCT + L'L	$d_\sigma + \pi_{\text{ppy}} \rightarrow \pi_{\text{ppy}}^*$
S ₁	448	436	0.0505	0.62 (125 \rightarrow 126) + 0.28 (125 \rightarrow 128)	MLCT + L'L	$d_\sigma + \pi_{\text{ppy}} \rightarrow \pi_{\text{ppy}}^*$
				...		
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Excited States in Transition Metal Complexes Used for DSSCs and Organic Light-Emitting Diodes

4. Obtain absorption, fluorescence, and phosphorescence band shapes for the salient excited states.
5. The emission lifetimes for $M(\text{bpy})_3^{2+}$ ($M = \text{Fe}, \text{Ru}, \text{and Os}$) are given in the table below:

Complex	Lifetime (ns)
$\text{Fe}(\text{bpy})_3^{2+}$	< 1
$\text{Ru}(\text{bpy})_3^{2+}$	~ 620
$\text{Os}(\text{bpy})_3^{2+}$	~ 20

Examine the radiative and non-radiative properties of these ions in terms of rapid and quantitative internal conversion/intersystem crossing through ligand-field states. Explain the experimental emission and non-emission lifetimes by considering calculated energy gaps in the d-orbital manifold, $d_\pi - \pi^*$ interaction, and solvent shifts.

Does the trend in d-orbital energies for this series of complexes follow the **Energy Gap Law**? Explain.

Why is the excited-state lifetime of $\text{Os}(\text{bpy})_3^{2+}$ so much shorter than that of $\text{Ru}(\text{bpy})_3^{2+}$, and why is the excited state lifetime of $\text{Fe}(\text{bpy})_3^{2+}$ so short?

6. Examine a structural distortion where M-L bonds are shortened or lengthened to assist in understanding absorption, fluorescence, and phosphorescence of these ions.

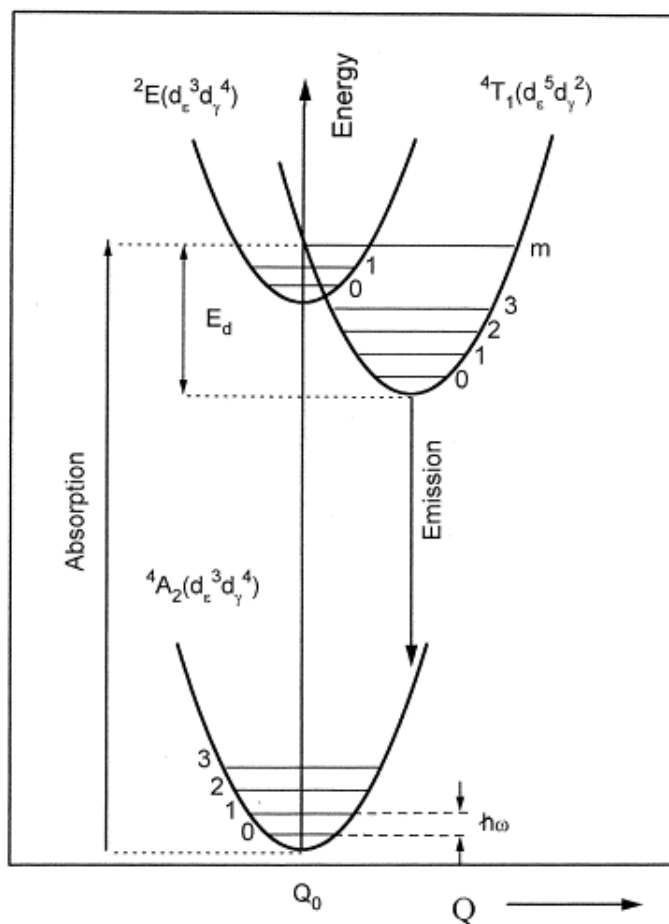


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The Franck-Condon Principle

The Franck-Condon (FC) Principle states that when a molecule is undergoing an electronic transition, the nuclear configuration of the molecule experiences no significant change. This is due in fact that nuclei are much more massive than electrons and the electronic transition takes place faster than the nuclei can respond. When the nucleus realigns itself with the new electronic configuration, it undergoes a vibration, and the FC principle provides a description of intensities of vibronic transitions, or the absorption or emission of a photon.



PES for Ground and Excited States



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The Franck-Condon Principle

In the figure above, the nuclear axis shows a consequence of the internuclear separation and the electronic transitions are indicated by the vertical arrows. The figure demonstrates three important points:

1. An absorption leads to a higher energy state.
2. Fluorescence leads to a lower energy state.

The fact that the fluorescence arrow is shorter than the absorption indicates that it has less energy, or that its wavelength is longer.

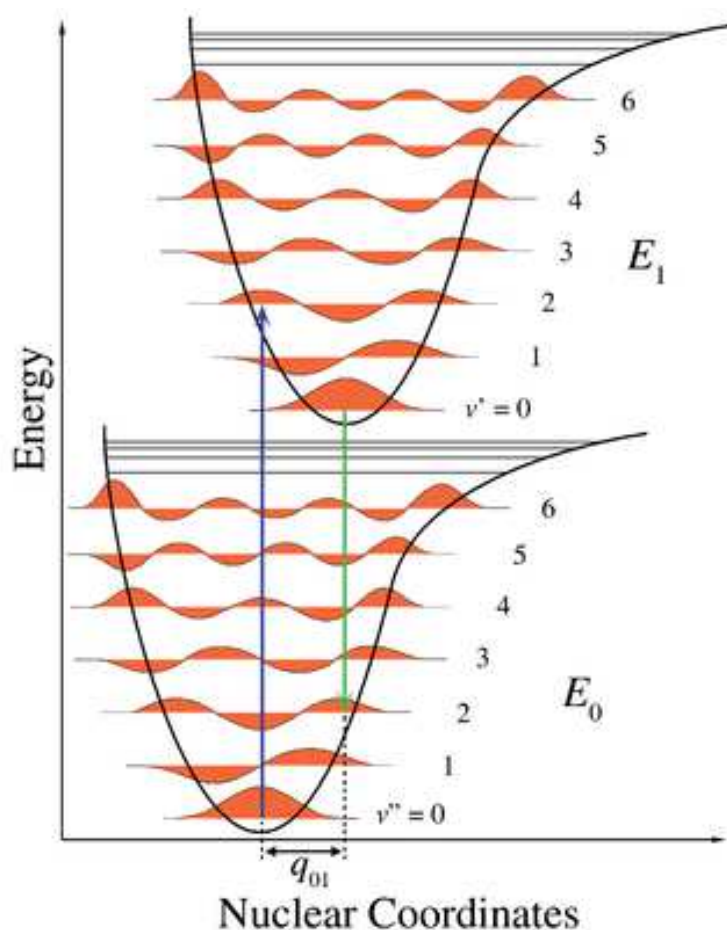
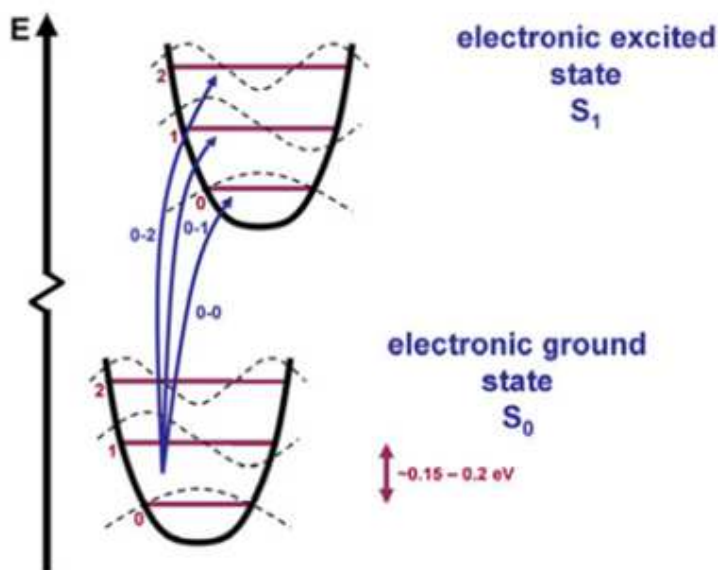
3. And the shift in nuclear coordinates between the ground and excited state is indicative of a new equilibrium position for nuclear interaction potential.



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the most intense transition is the vertical one

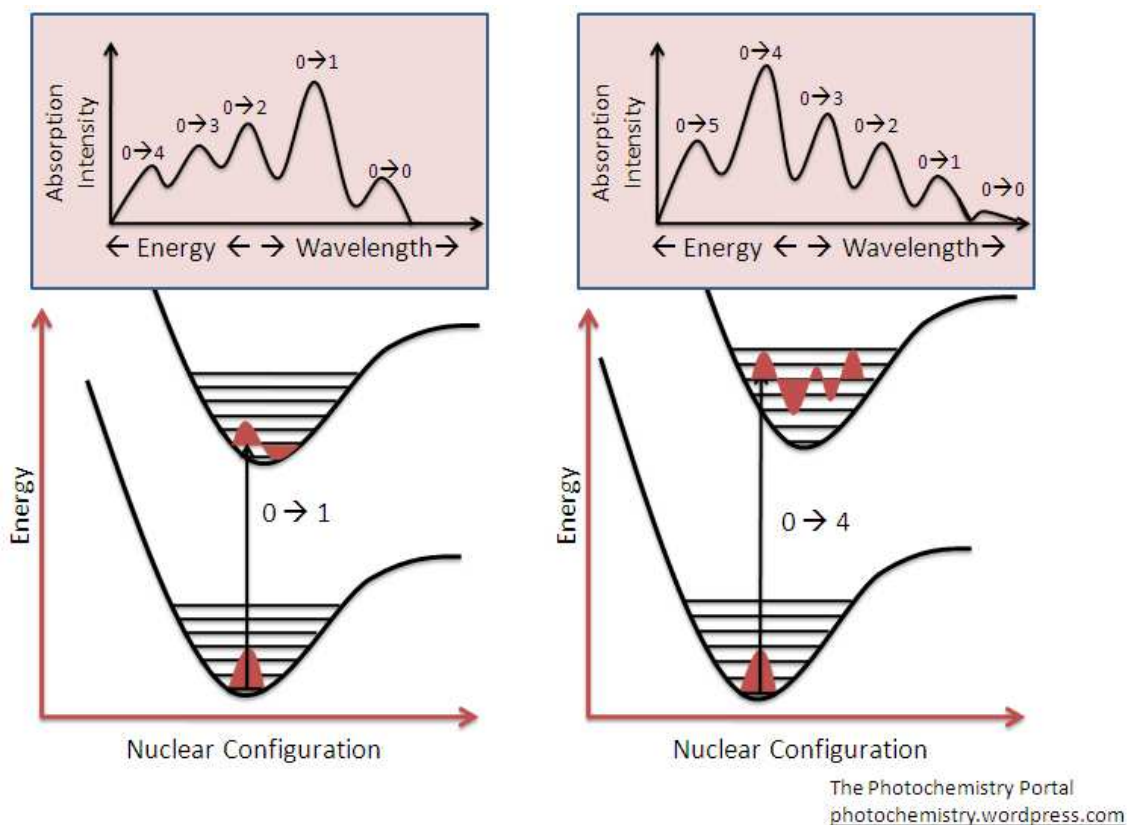


Franck-Condon Transition Showing Origin Shift of Excited PES



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Absorption Spectra With Underlying Vibrational Structure



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Overview of Electronic Spectroscopy

A molecule that is excited with the absorption of an electron to an excited state can return to the ground state by several combinations of mechanical steps that will be described below and is shown in the figure: The deactivation processes of fluorescence and phosphorescence involve an emission of a photon radiation as shown by the straight arrows in the figure below.

- Absorption transitions can occur from the ground singlet electronic state (S_0) to various vibrational levels in the singlet excited vibrational states (S_1, S_2, \dots, S_n).
- Fluorescence involves absorption of photons from the singlet ground state promoted to a singlet excited state. As the excited molecule returns to ground state, it involves the emission of a photon of lower energy, which corresponds to a longer wavelength, than the absorbed photon.
- The wiggly arrows in the figure are deactivation processes without the use of radiation and is called internal conversion (IC).

Internal conversion is an intermolecular process of molecule that passes to a lower electronic state without the emission of radiation.

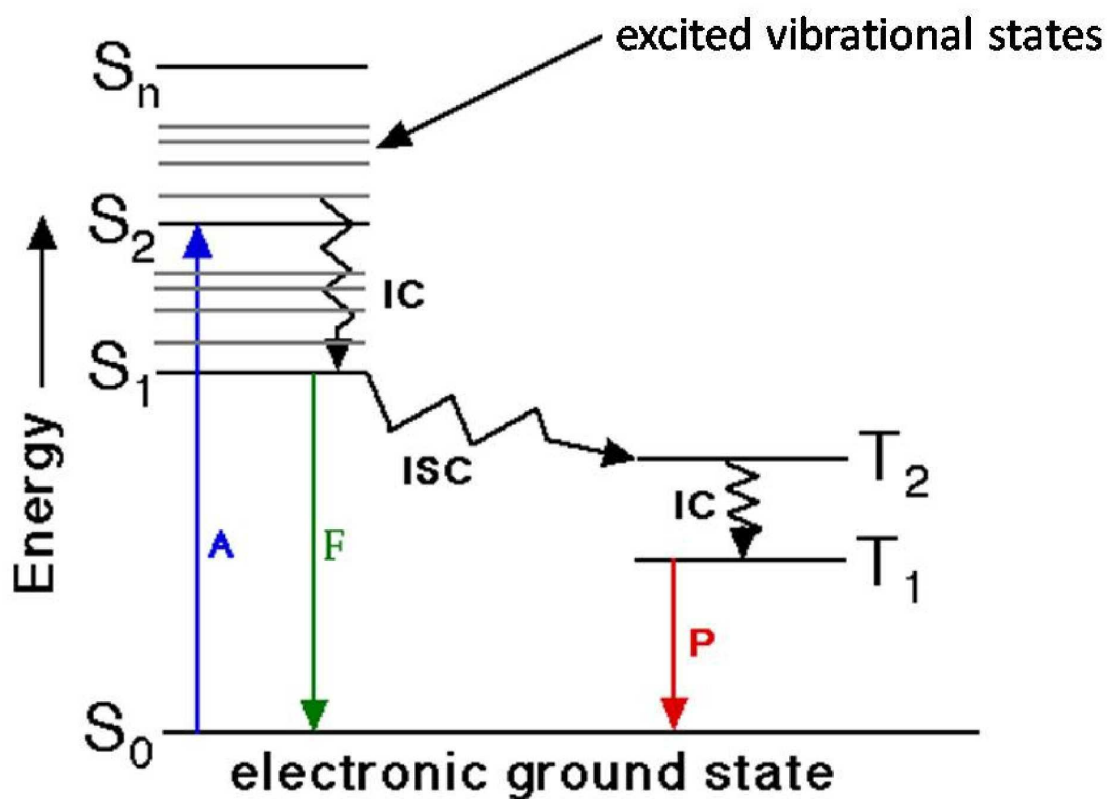
- Intersystem crossing is a process where there is a crossover between electronic states of different multiplicity as demonstrated in the singlet state to a triplet state
- After the molecule transitions through intersystem crossing to the triplet state, further deactivation occurs through phosphorescence. ($S_1 \rightarrow T_2 \rightarrow T_1$)



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Overview of Electronic Spectroscopy



Absorption, Fluorescence, and Phosphorescence



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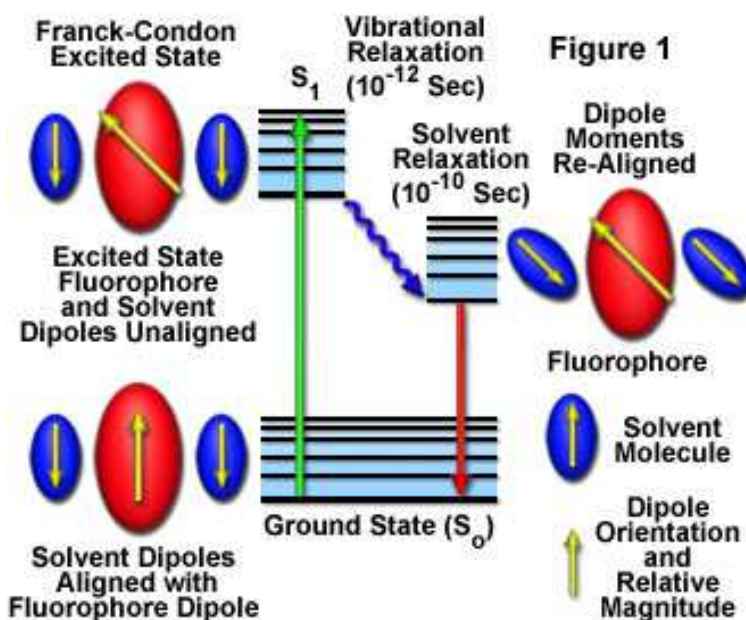
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Solvent Effects on the Excited States of Molecules

A variety of environmental factors affect excitation of molecules including interactions between the solute molecule and surrounding solvent molecules which is related to solvent polarity, temperature, pH, and the localized concentration of the solute molecule.

In solution, solvent molecules surrounding the solute molecules have dipole moments that can interact with the dipole moment of the solute to yield an ordered distribution of solvent molecules around the solute. Differences between the ground and excited states in the solute molecule produce a change in the molecular dipole moment, which ultimately induces a rearrangement of surrounding solvent molecules.

However, the Franck-Condon principle dictates that, upon excitation of molecule, the molecule is excited to a higher electronic energy level in a far shorter time frame than it takes for the solute and solvent molecules to re-orient themselves within the solvent-solute interactive environment. As a result, there is a time delay between the excitation event and the re-ordering of solvent molecules around the solvated solute as illustrated in the figure below, which generally has a much larger dipole moment in the excited state than in the ground state.



Solute-Solvent Excited-Excited State Interactions



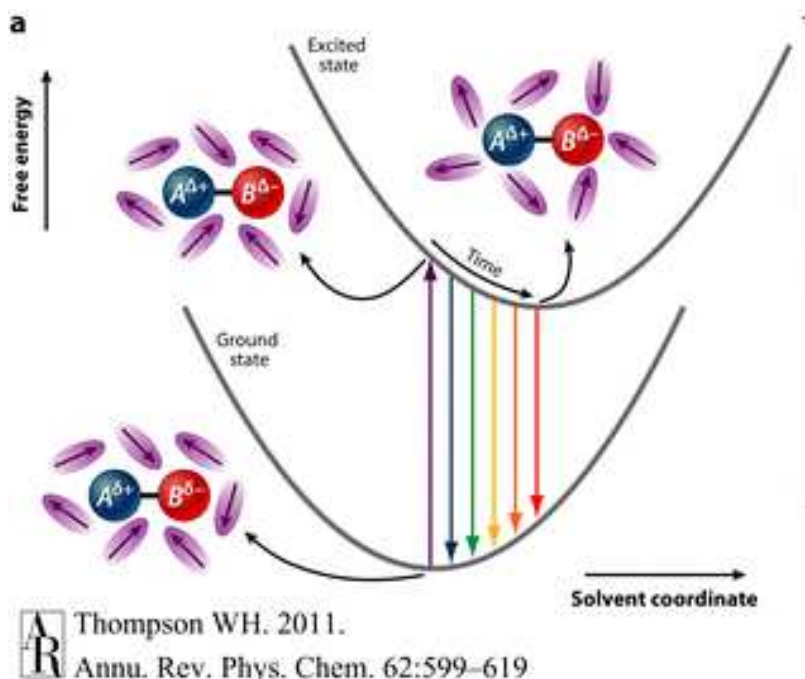
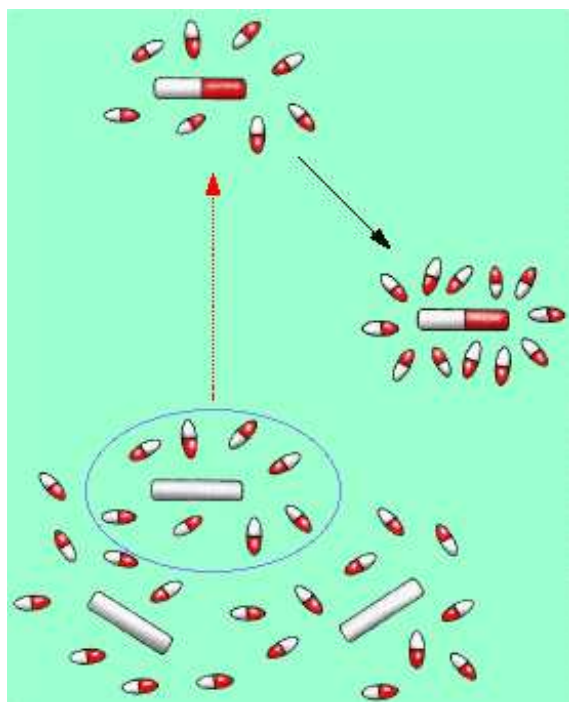
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Solvent Effects on the Excited States of Molecules

After the solute has been excited to higher vibrational levels of the an excited singlet state S_n , excess vibrational energy is rapidly lost to surrounding solvent molecules as the solute slowly relaxes to the lowest vibrational energy level occurring in the picosecond time scale. Solvent molecules assist in stabilizing and further lowering the energy level of the excited state by re-orienting (solvent relaxation) around the excited solute in a slower process that requires between 10 and 100 picoseconds.

This has the effect of reducing the energy separation between the ground and excited states, which results in a red shift (to longer wavelengths) of the fluorescence emission. Increasing the solvent polarity produces a correspondingly larger reduction in the energy level of the excited state, while decreasing the solvent polarity reduces the solvent effect on the excited state energy level. The polarity of the solute molecule also determines the sensitivity of the excited state to solvent effects. Polar and charged solute molecules exhibit a far stronger effect than non-polar solvent molecules.



Thompson WH. 2011.
Annu. Rev. Phys. Chem. 62:599-619

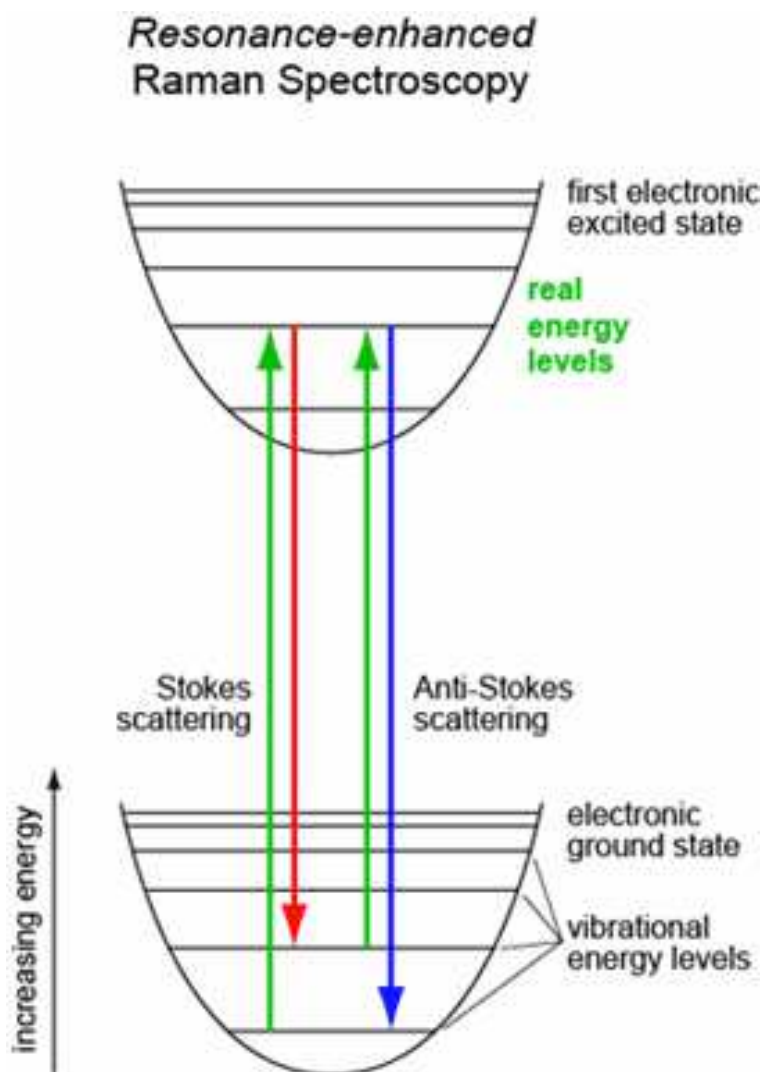
Two Views of Excited-State Solvent Re-Orientation



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Solvent relaxation effects on fluorescence can result in a dramatic effect on the size of Stokes shifts. Fluorescence and phosphorescence emission can result in a red-shift of 10-200 nm due to solvent effects. Thus, the emission spectra of both intrinsic and extrinsic fluorescent probes can be employed to probe solvent polarity effects, molecular associations, and complex formation with polar and non-polar small molecules and macromolecules.



Stokes and Anti-Stokes Shifts