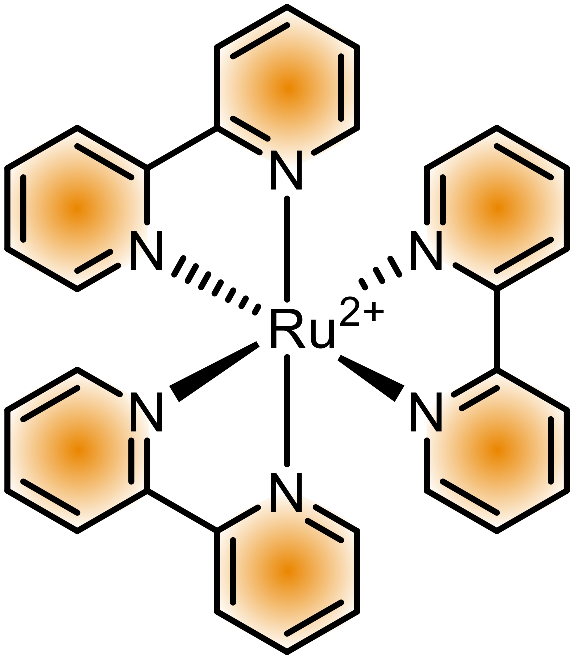
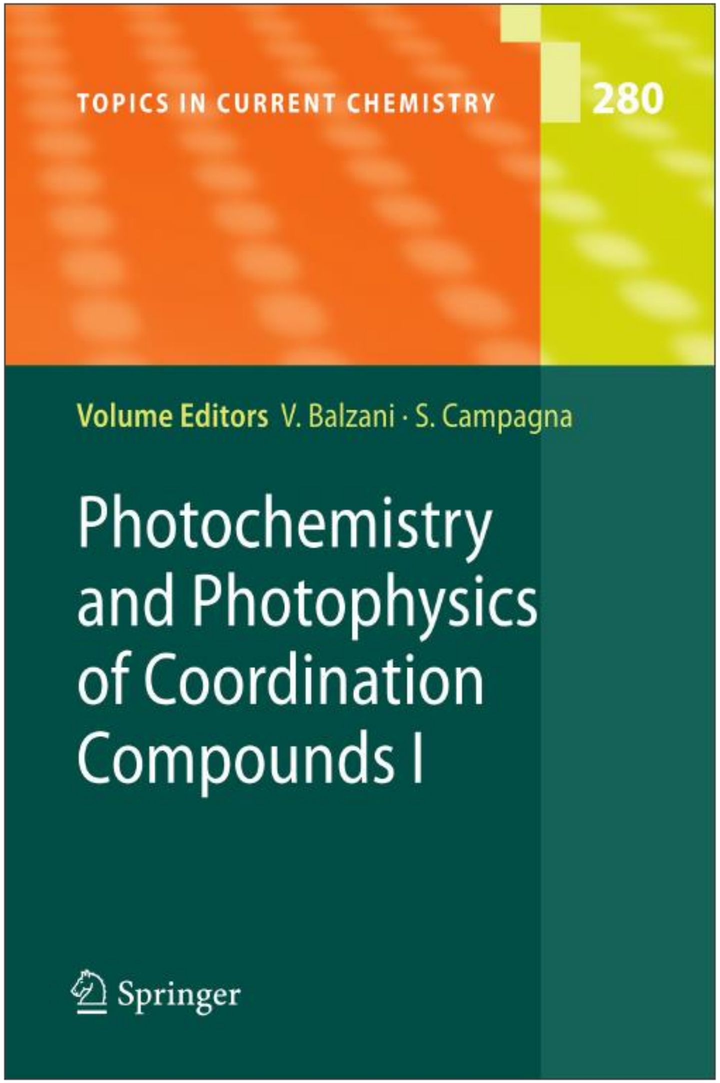
The Photochemistry of $Ru(bpy)_3^{2+}$



CHEM 6420

Primary Reference



TOPICS IN CURRENT CHEMISTRY 280

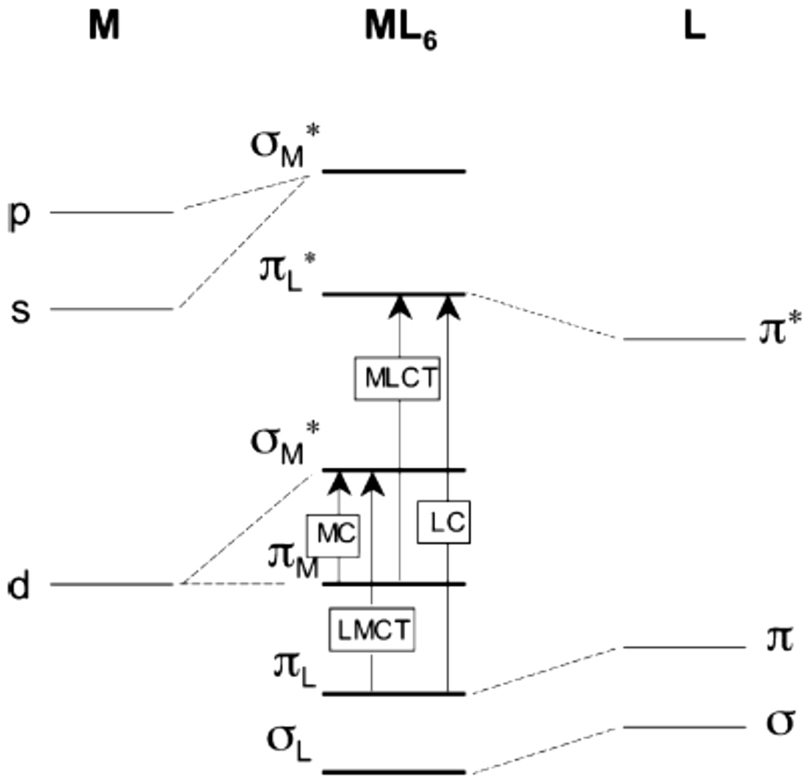
Volume Editors V. Balzani · S. Campagna

Photochemistry and Photophysics of Coordination Compounds I

Springer

Photochemistry of Metal Complexes

- For metal complexes, the construction of Jablonski diagrams via electronic configurations from the MO description follows the same general lines described in Chapter 1 of this course for organic molecules
- A schematic MO diagram for an octahedral transition metal complex is shown below:



Photochemistry of Metal Complexes

- The various MOs can be conveniently classified according to their predominant atomic orbital contributions as:

1) Strongly bonding, predominantly ligand-centered σ_L orbitals
2) Bonding, predominantly ligand-centered π_L orbitals
3) Essentially nonbonding, metal-centered π_M orbitals of t_{2g} symmetry
4) Antibonding, predominantly metal-centered σ^*_M orbitals of e_g symmetry
5) Antibonding, predominantly ligand-centered π^*_L orbitals
6) Strongly antibonding, predominantly metal-centered σ^*_M orbitals

- In the ground electronic configuration of an octahedral complex of a d^n metal ion, orbitals of type 1 and 2 are filled, while n electrons reside in the orbitals of types 3 and 4

Recap: Octahedral Metal Complexes

- The *d* orbital splitting is defined as the pattern of energies of the d orbitals, and it results from the geometry of the complex
- You might recall from inorganic chemistry that *crystal field theory* predicts the splitting
- A general rule for predicting splitting is that d orbitals that lie along the bonds to the ligands are raised in energy, and the d orbitals that do not lie along the bond axes are relatively unperturbed in energy
- For an octahedral complex (6 ligands around a metal ion), the d orbitals are split into two sets, where the d_{xy}, d_{xz}, and d_{yz} orbitals are lower in energy and the d_{z^2} and $d_{x^2-y^2}$ orbitals are higher in energy
- The three lower-energy orbitals are collectively referred to as t_{2g}, and the two higher-energy orbitals as e_g

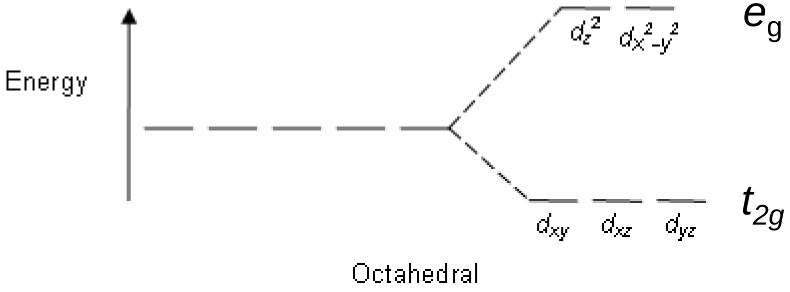
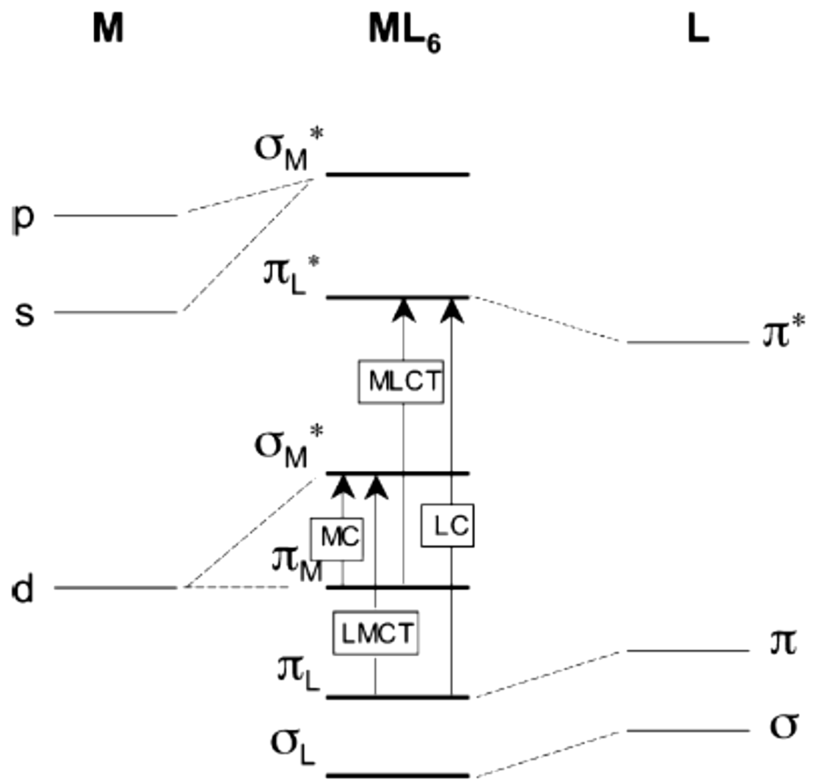


Image source: Wikipedia

Photochemistry of Metal Complexes



- For metal complexes, one expects to find transitions of the following types:

1) *Metal-centered* (MC) transitions of type 3 → 4

2) *Ligand-centered* (LC) transitions of type 2 → 5

3) *Ligand-to-metal charge-transfer* (LMCT) transitions, e.g., type 2 → 4

4) *Metal-to-ligand charge-transfer* (MLCT) transitions, e.g., type 3 → 5

Photochemistry of Metal Complexes

The relative energy ordering depends on the nature of the metal and ligands

- Low-energy MC transitions are expected for first-row transition-metals

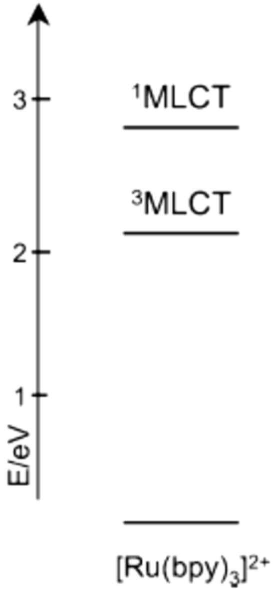
- Low-energy LMCT transitions are expected when at least one of the ligands is easy to oxidize and the metal is easy to reduce

- Low-energy MLCT transitions are expected when the metal is easy to oxidize and a ligand is easy to reduce

- Low-energy LC transitions are expected for aromatic ligands with extended π and π^* orbitals

Photochemistry of Metal Complexes

- For octahedral complexes of Ru(II), and the other d^6 metal ions, the σ_L and π_L orbitals are fully occupied and the ground-state configuration is closed-shell since the HOMO, $\pi_M(t_{2g})^6$, is also completely occupied
- The ground state is therefore a singlet, and the excited states are either singlet or triplet in nature, similar to the organic molecules we've previously studied
- In the case of $[Ru(bpy)_3]^{2+}$, since Ru(II) is easy to oxidize and the 2,2'-bipyridine ligands are easy to reduce, the lowest triplet and singlet excited states are MLCT character



Bimolecular Processes

- In fluid solution, when the excited state is sufficiently long, an excited molecule *R may have a chance to encounter another molecule, M

- In such a case, some specific interaction can occur leading to the deactivation of *R by second-order kinetic processes

- The most important types of interactions in an encounter are those leading to electron- or energy-transfer

$^*R + M \rightarrow R^{\bullet +} + M^{\bullet -}$ *Oxidative electron-transfer*

$^*R + M \rightarrow R^{\bullet -} + M^{\bullet +}$ *Reductive electron-transfer*

$^*R + M \rightarrow R + {}^*M$ *Energy transfer*

Bimolecular Processes

- Reminder: an excited state is both a stronger reductant and stronger oxidant than the corresponding ground state (Chapter 7)

- The redox potentials of the excited state may be calculated from the ground state oxidation and reduction potentials and the one-electron potential corresponding to the zero–zero excited state energy, E^{0-0}, as shown by eq 1 and 2:

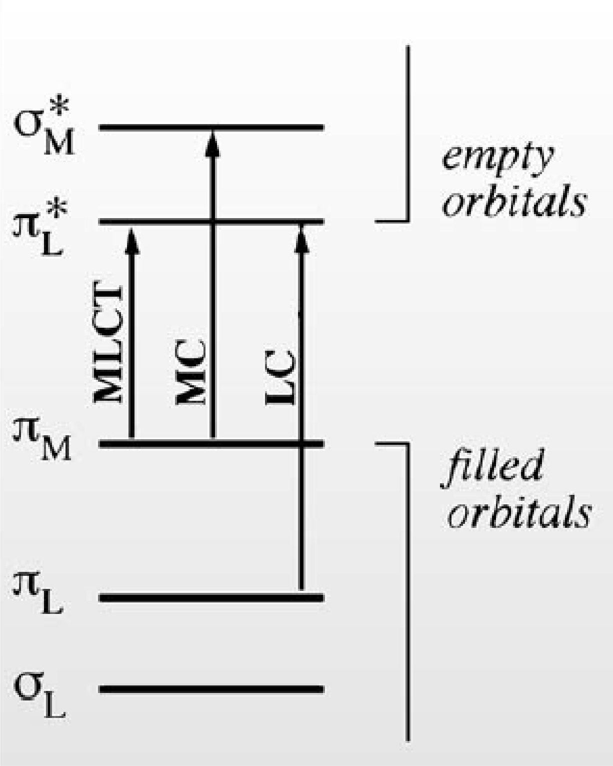
$$E(\mathrm{R}^{\bullet+}/{*\mathrm{R}}) \approx E(\mathrm{R}^{\bullet+}/\mathrm{R}) - E^{0-0} \quad (1)$$

$$E({*\mathrm{R}}/\mathrm{R}^{\bullet-}) \approx E(\mathrm{R}/\mathrm{R}^{\bullet-}) + E^{0-0} \quad (2)$$

Structure, Bonding, and Excited States of Ru(II)L_6 Complexes

- Ru^{2+} is a d^6 system and the polypyridine ligands are usually colorless molecules possessing σ donor orbitals localized on the nitrogen atoms and π donor and π^* acceptor orbitals delocalized on aromatic rings

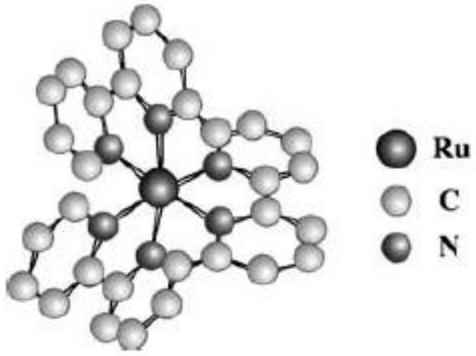
- The figure below is a simplified MO diagram of Ru(II) polypyridine complexes showing the possible electronic transitions

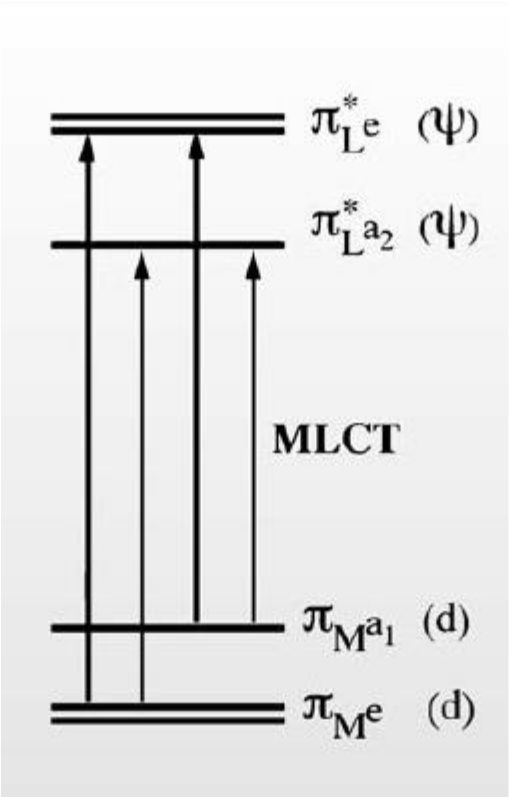


Structure, Bonding, and Excited States of Ru(II)L_6 Complexes

- $Ru(bpy)_3^{2+}$, as well as most of the $Ru(LL)_3^{2+}$ complexes (LL = bidendate polypyridine ligand), exhibits a D_3 symmetry

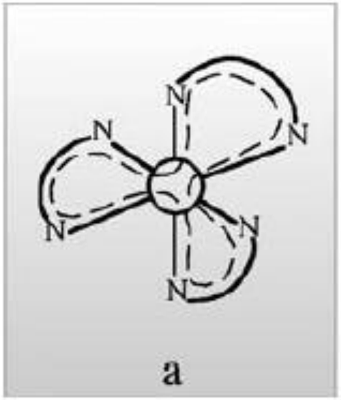
- A more detailed picture of the MO diagram is shown below



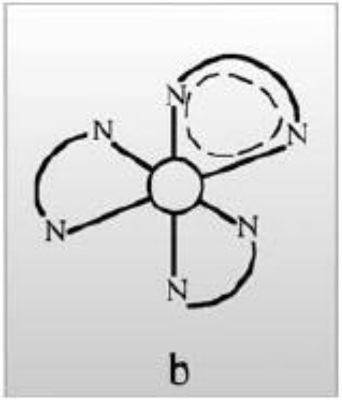


Structure, Bonding, and Excited States of Ru(II)L_6 Complexes

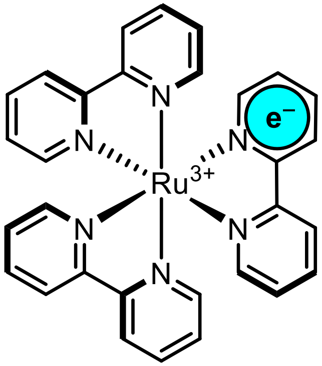
- For most Ru(II) polypyridine complexes, *the lowest excited state is a* ^{3}MLCT *state* which undergoes relatively slow radiationless transitions and thus exhibits relatively a long lifetime and intense luminescence emission
- Such a state is obtained from promoting an electron from a metal π_M orbital to a ligand π^*_L orbital
- The same π^*_L orbital is usually involved in one-electron reduction processes
- It has long been discussed whether in homoleptic complexes the emitting ^{3}MLCT state is best described with a multi-chelate ring-delocalized orbital (a) or a single chelate ring-delocalized orbital (b), but *there is compelling evidence of "spatially isolated" redox orbitals* (b)



a



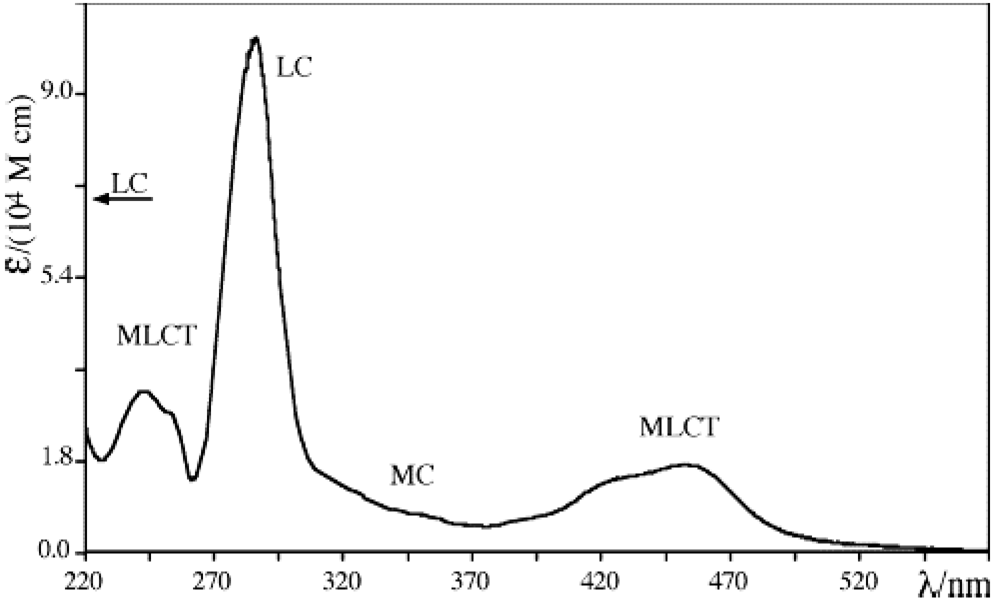
b



^{3}MLCT

$Ru(bpy)_3^{2+}$: Absorption Spectrum

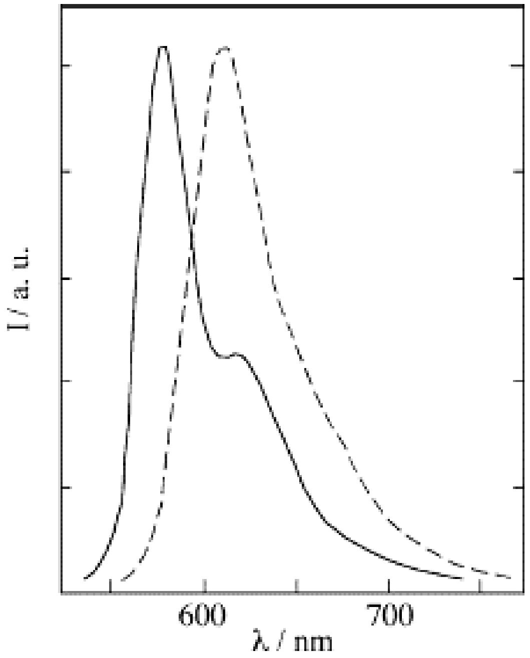
- The absorption spectrum of $Ru(bpy)_3^{2+}$ is shown below along with the proposed assignments



- The bands at 185 nm (not shown) and 285 nm have been assigned as spin-allowed LC π → π* transitions by comparison with the spectrum of protonated bipyridine
- The two remaining intense bands at 240 and 450 nm have been assigned to spin-allowed MLCT d → π* transitions

$Ru(bpy)_3^{2+}$: Emission Properties

- Excitation of $Ru(bpy)_3^{2+}$ in any of its absorption bands leads to a luminescence emission whose intensity, lifetime, and energy position are more or less temperature dependent
- Detailed studies on the temperature dependence showed that luminescence originates from three closely spaced levels in thermal equilibrium
- This cluster of luminescent, closely spaced excited states will be indicated in the following by $^*Ru(bpy)_3^{2+}$ or as the ^{3}MLCT state



$Ru(bpy)_3^{2+}$: Emission Properties

- In rigid glass at 77 K the emission lifetime of $^*Ru(bpy)_3^{2+}$ is ~ 5 μs and the emission quantum yield is ~ 0.4

- Taken together with the unitary intersystem crossing efficiency, these figures yield a value of ~ 13 μs for the radiative lifetime

- Values of this order of magnitude have been found for MLCT states of other transition metal complexes

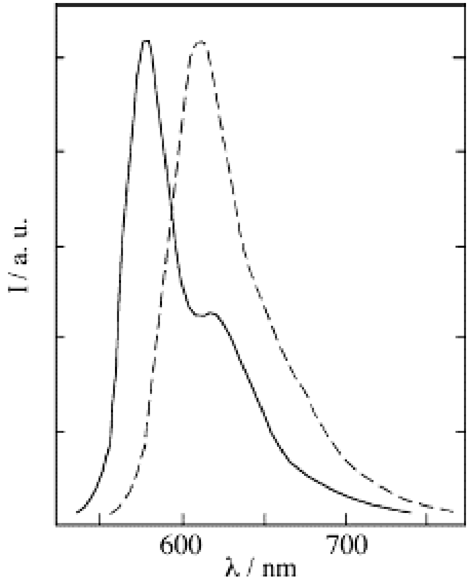
- LC excited states of transition metal complexes usually exhibit radiative lifetimes in the millisecond range

Ru(bpy)$_3^{2+}$: Emission Properties

- In the 77 K emission spectrum of Ru(bpy)$_3^{2+}$, there is some vibrational structure

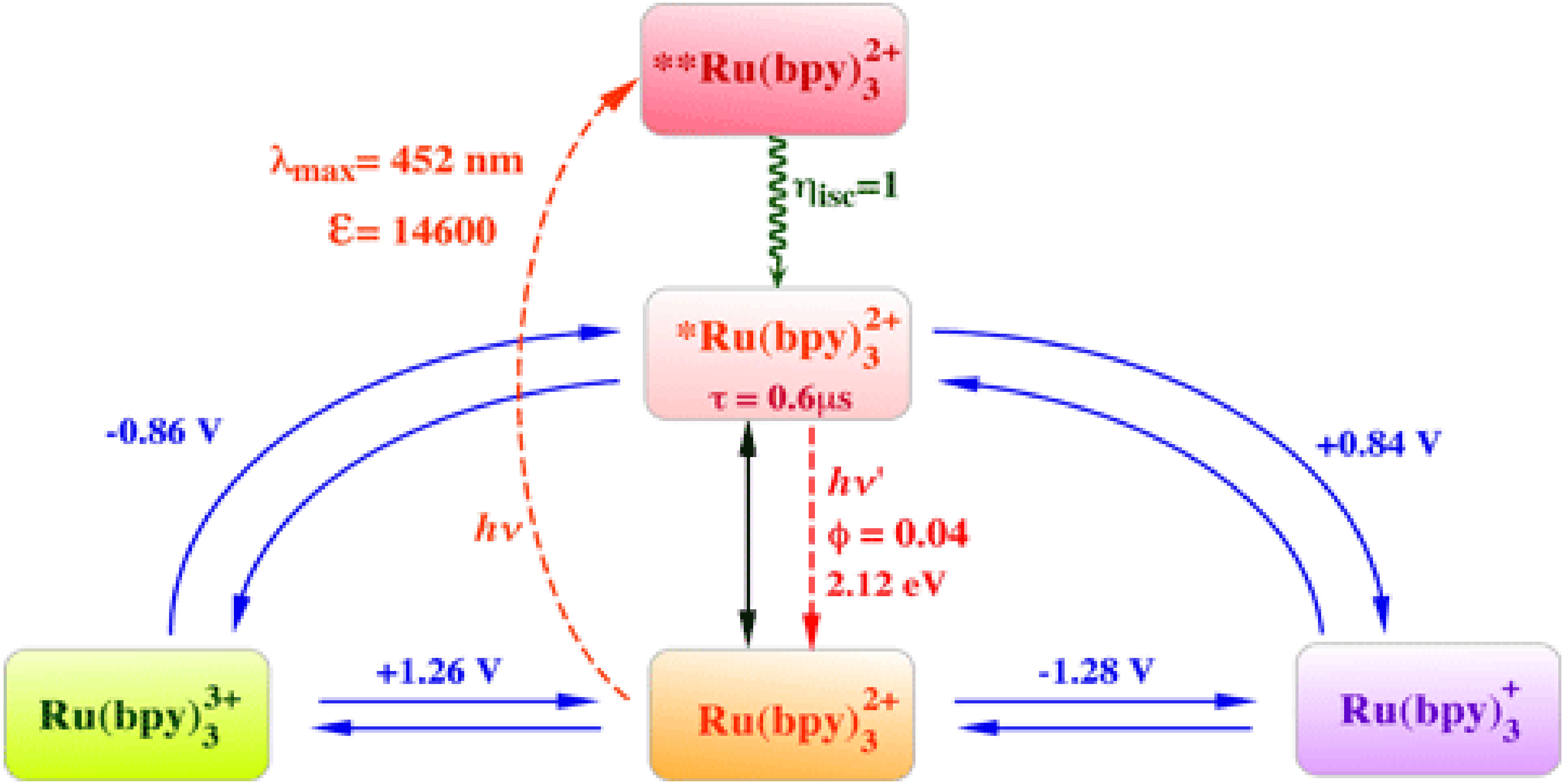
- This structure has been assigned to the C–N and C–C stretching of the aromatic rings

- This provides an indication of the dominant modes for deactivation of the ^{3}MLCT state



Quenching of the ^{3}MLCT Excited State

- The lowest ^{3}MLCT excited state of $Ru(bpy)_3^{2+}$ lives long enough to encounter other solute molecules (even when present at relatively low concentrations) and possesses suitable properties to play the role of energy donor, electron donor, or electron acceptor



Quenching of the ^{3}MLCT Excited State

- The energy available to $*\mathrm{Ru(bpy)_3^{2+}}$ for energy transfer processes is 2.12 eV, or 49 kcal mol^{-1}

- The reduction and oxidation potentials are + 0.84 and -0.86 V (aqueous solution, vs. SCE)

$*\mathrm{Ru^{II}(bpy)_3^{2+}} + \mathrm{Q} \rightarrow \mathrm{Ru^{II}(bpy)_3^{2+}} + *\mathrm{Q}$ *energy transfer*

$*\mathrm{Ru^{II}(bpy)_3^{2+}} + \mathrm{Q} \rightarrow \mathrm{Ru^{III}(bpy)_3^{3+}} + \mathrm{Q^{\bullet -}}$ *oxidative quenching*

$*\mathrm{Ru^{II}(bpy)_3^{2+}} + \mathrm{Q} \rightarrow \mathrm{Ru^{II}(bpy)_2(bpy^{\bullet -})^{+}} + \mathrm{Q^{\bullet +}}$ *reductive quenching*

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