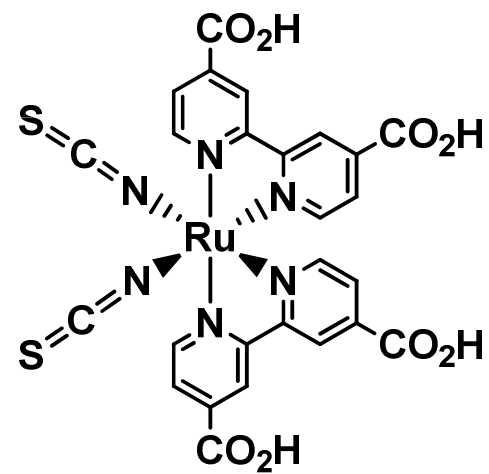
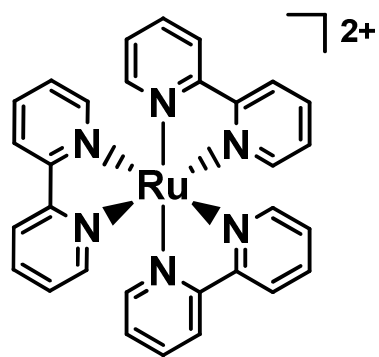
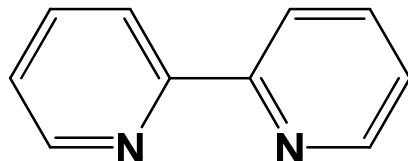


Ruthenium Polypyridyl Photochemistry

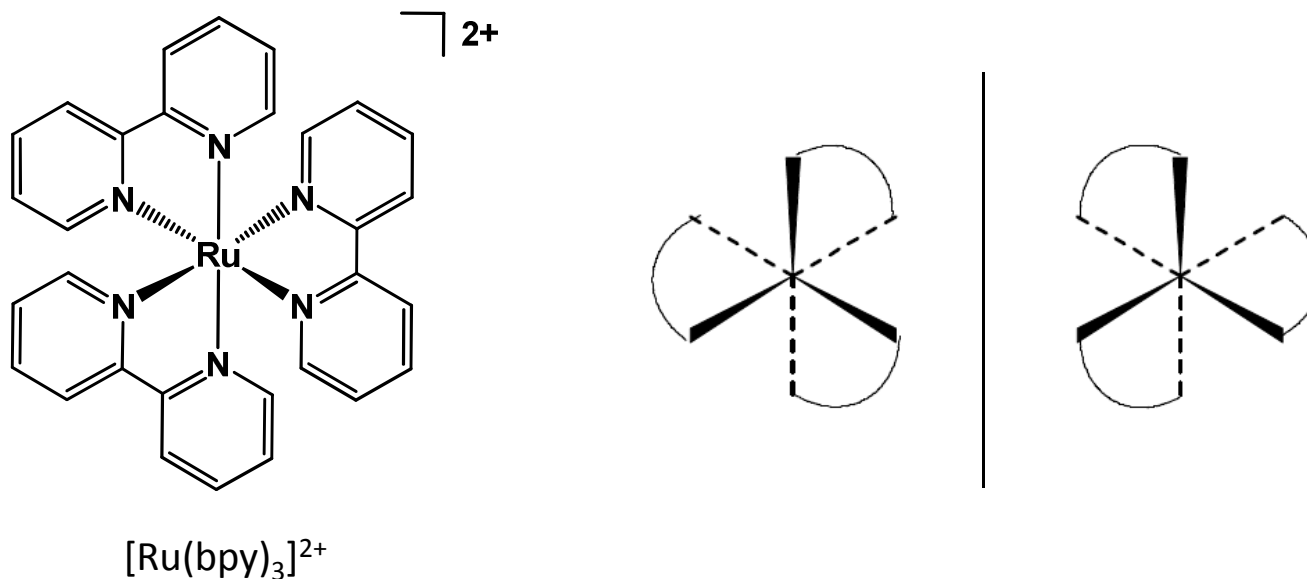


2,2'-Bipyridine

- 2,2'-bipyridine, commonly abbreviated as *bpy*, functions as a bidentate chelating ligand.



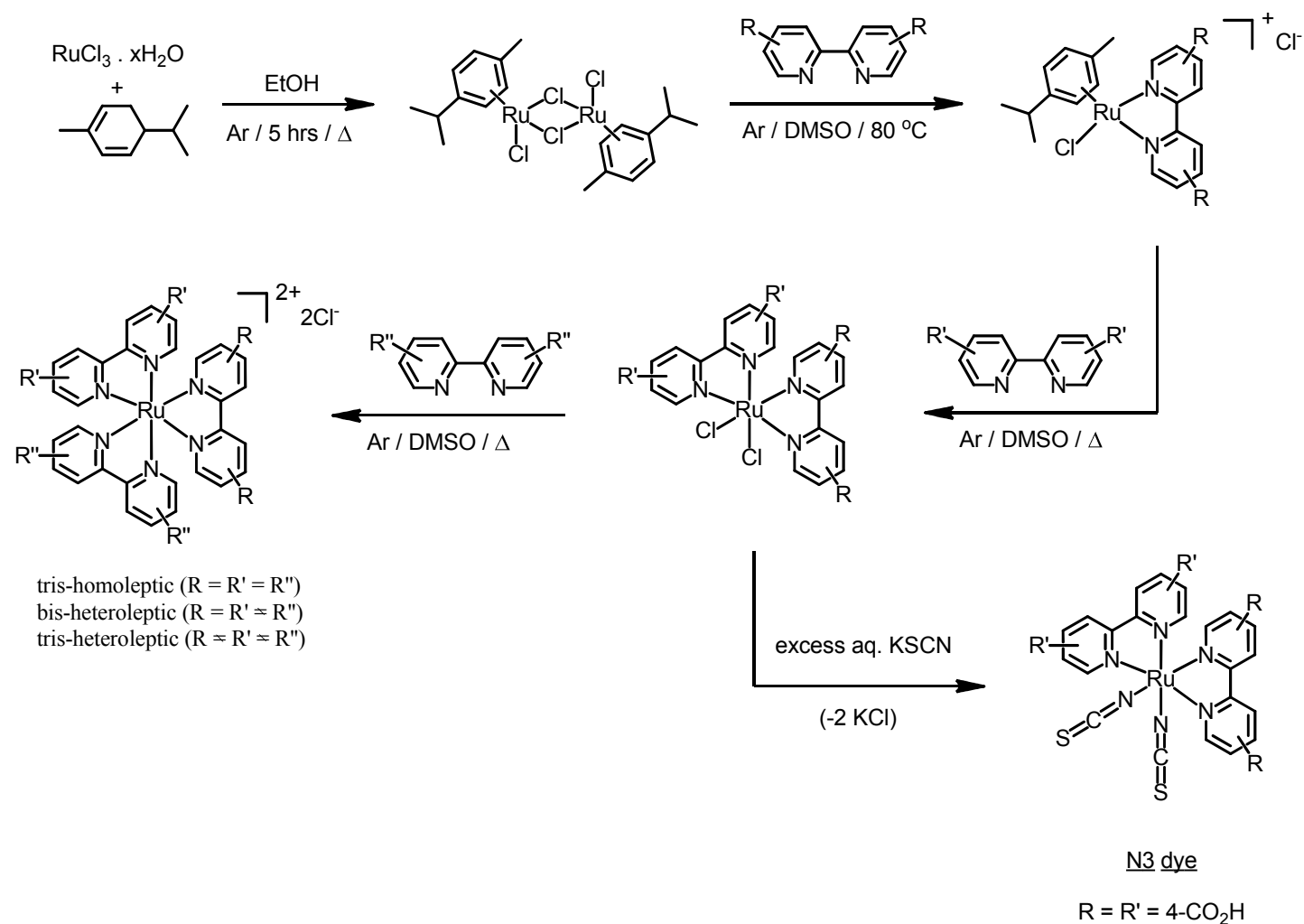
- The $[\text{Ru}(\text{bpy})_3]^{2+}$ complex is actually a mixture of two optical isomers with D_3 symmetry.



[Ru(bpy)₃]²⁺ Electronic Structure

- Second-row transition ions, like Ru²⁺ tend to have larger Δ_0 values and smaller P values.
- Also, bpy is a strong-field ligand, which tends to produce large Δ_0 values.
- As a result, [Ru(bpy)₃]²⁺ is a d^6 low-spin case, which is diamagnetic.
- [Ru(bpy)₃]²⁺ has two absorption bands at 428 nm and 454 nm with high extinction coefficients which have been assigned to *metal-ligand charge-transfer* (MLCT) transitions
- The absorption of the blue end of the spectrum gives the complex its characteristic red color.
- [Ru(bpy)₃]²⁺ can be made to show *chemiluminescence*.

N3 synthesis



Scheme 1. Stepwise synthesis of a tris-heteroleptic ruthenium(II) polypyridyl complex using the dichloro(*p*-cymene)ruthenium(II) dimer precursor.

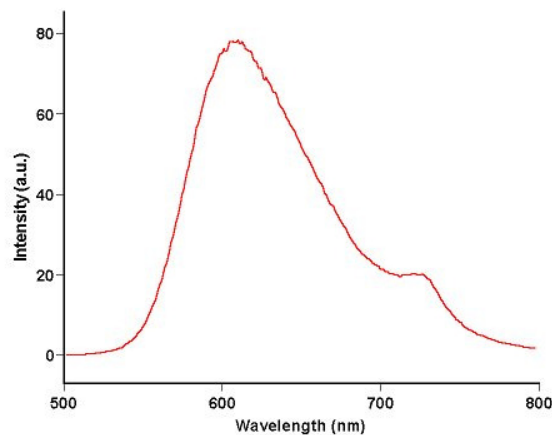
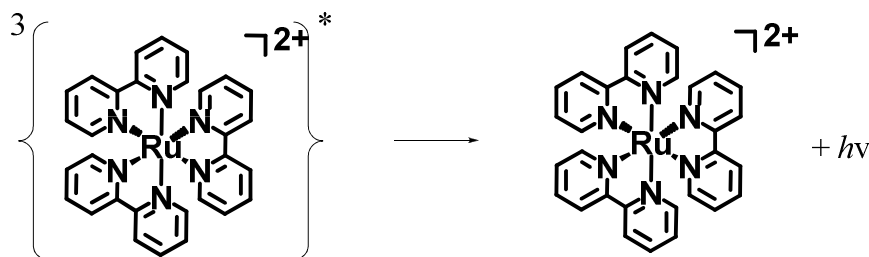
Chemiluminescence

- *Chemiluminescence* is the production of visible light through a *chemically induced excited state* of a molecule, which relaxes back to the ground state by photon emission.
- *Fluorescence* is a short lifetime *photoluminescence* process (0.5-20 ns) in which a molecule emits a photon from a singlet excited state, thus quickly decaying back to its singlet ground state.
- Both the ground and excited states are singlet states ($m = 2S + 1$ where $S = 0$).

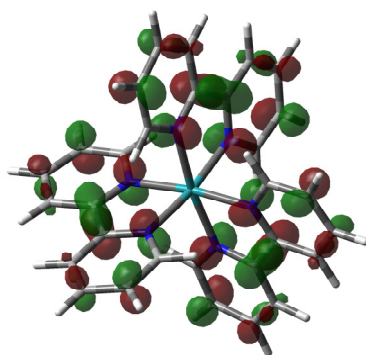


- ${}^1M^*$ can also lose energy by non-radiative processes (thermal motion, vibration, molecular quenching), resulting in no light emission, i.e. non-radiative decay.

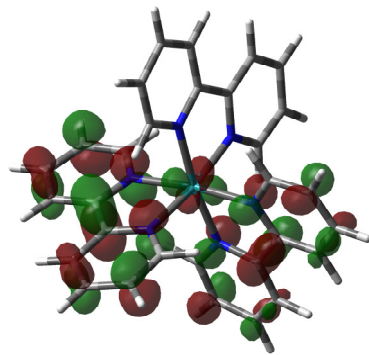
- *Phosphorescence* is a longer lifetime *photoluminescence* process (μs - hours) in which the excited molecule undergoes an intersystem crossing (*isc*) to a triplet excited state.
- Radiative transition from an excited triplet state to the singlet ground state is quantum mechanically “forbidden” but occurs with low efficiency, resulting in longer lifetimes.



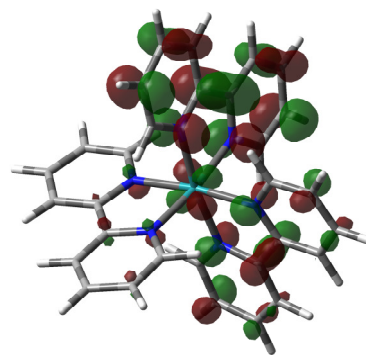
Molecular Orbitals of $[\text{Ru}(\text{bpy})_3]^{2+}$



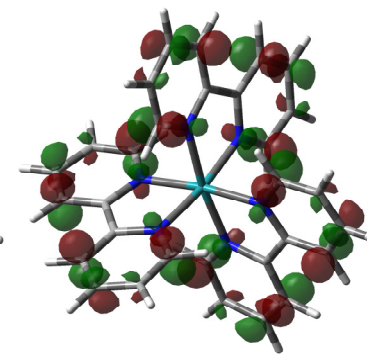
LUMO



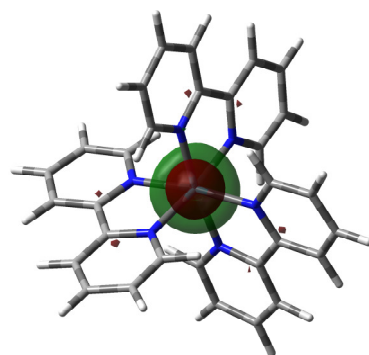
LUMO+1



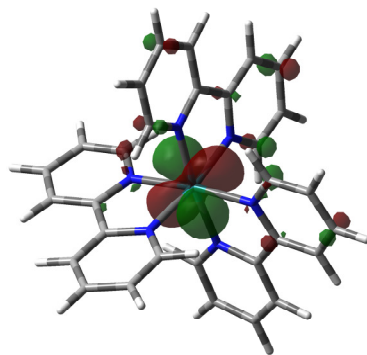
LUMO+2



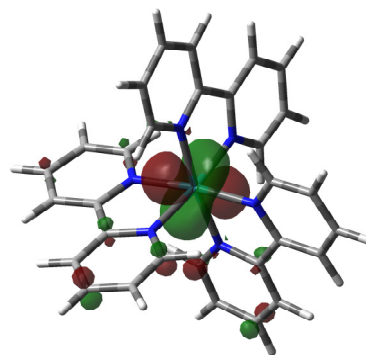
LUMO+5



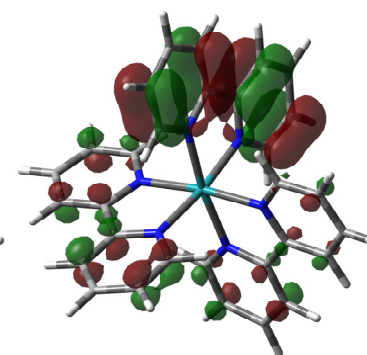
HOMO



HOMO-1

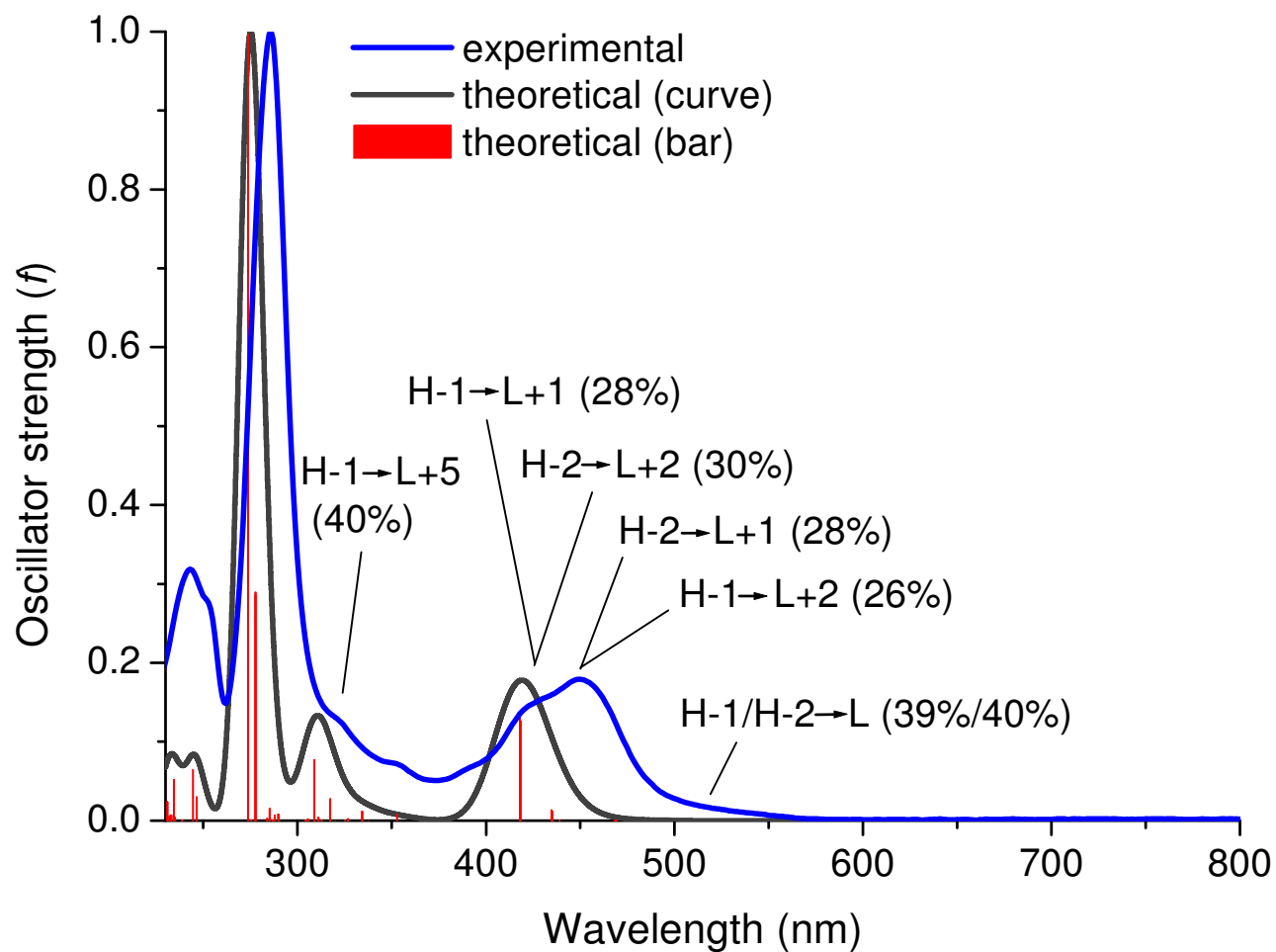


HOMO-2

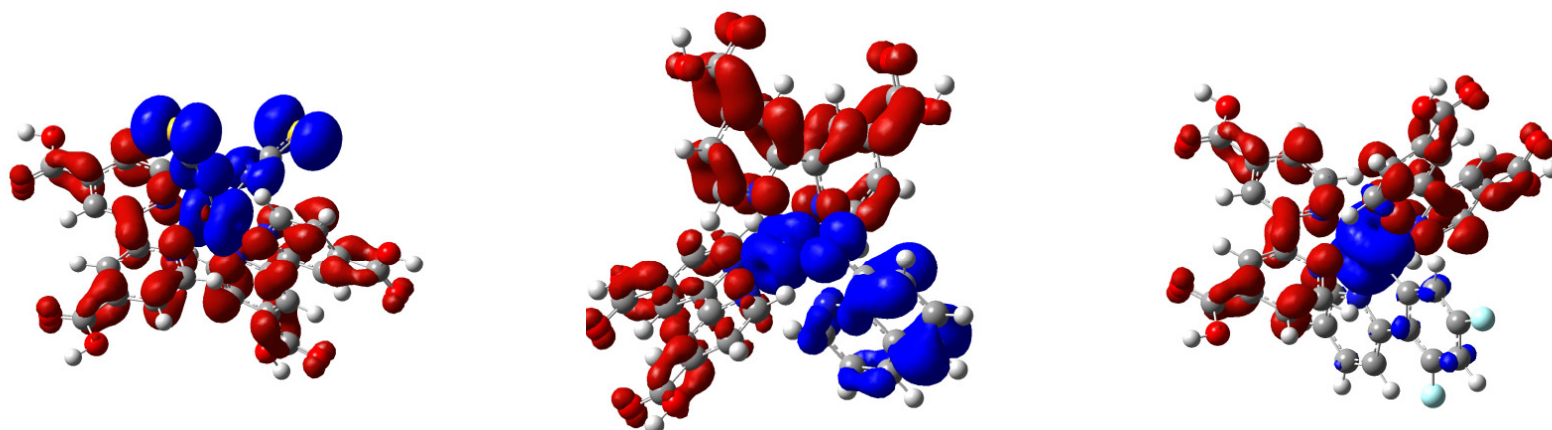


HOMO-3

Experimental and Computational UV-vis spectra for $[\text{Ru}(\text{bpy})_3]^{2+}$



Non-Innocent Ligand Architectures for Dye Sensitized Solar Cell Applications



Jonathan Rochford

Center for Green Chemistry, **Department of Chemistry**



*International Materials Institute for Solar Energy and Environment
Xiamen University, PRC, Oct. 25th 2011*

Splitting of d orbital degeneracies : $O_h \rightarrow D_{4h}$

- From the correlation table that links the groups O_h and D_{4h} we see that the two e_g orbitals of the octahedral field become non-degenerate as a_{1g} and b_{1g} in the tetragonal field.

- From the direct product listings in the D_{4h} character table we see

$$a_{1g} = d2z^2-x^2-y^2 (= dz^2)$$

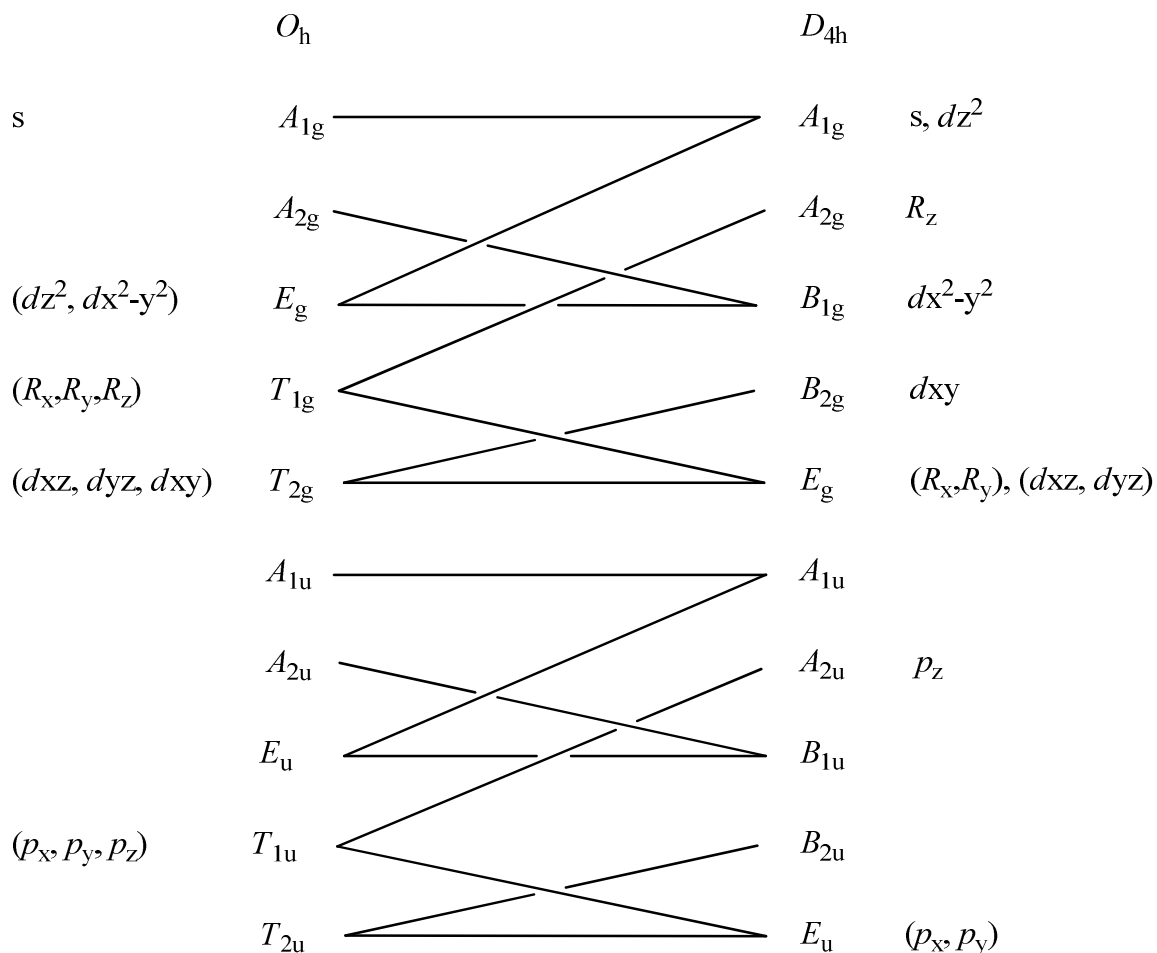
$$b_{1g} = dx^2-y^2$$

- The degeneracy among the t_{2g} orbitals in O_h is partially lifted to become b_{2g} and e_g in the D_{4h} tetragonal field.

- From the direct product listings in the D_{4h} character table we see

$$b_{2g} = dxy$$

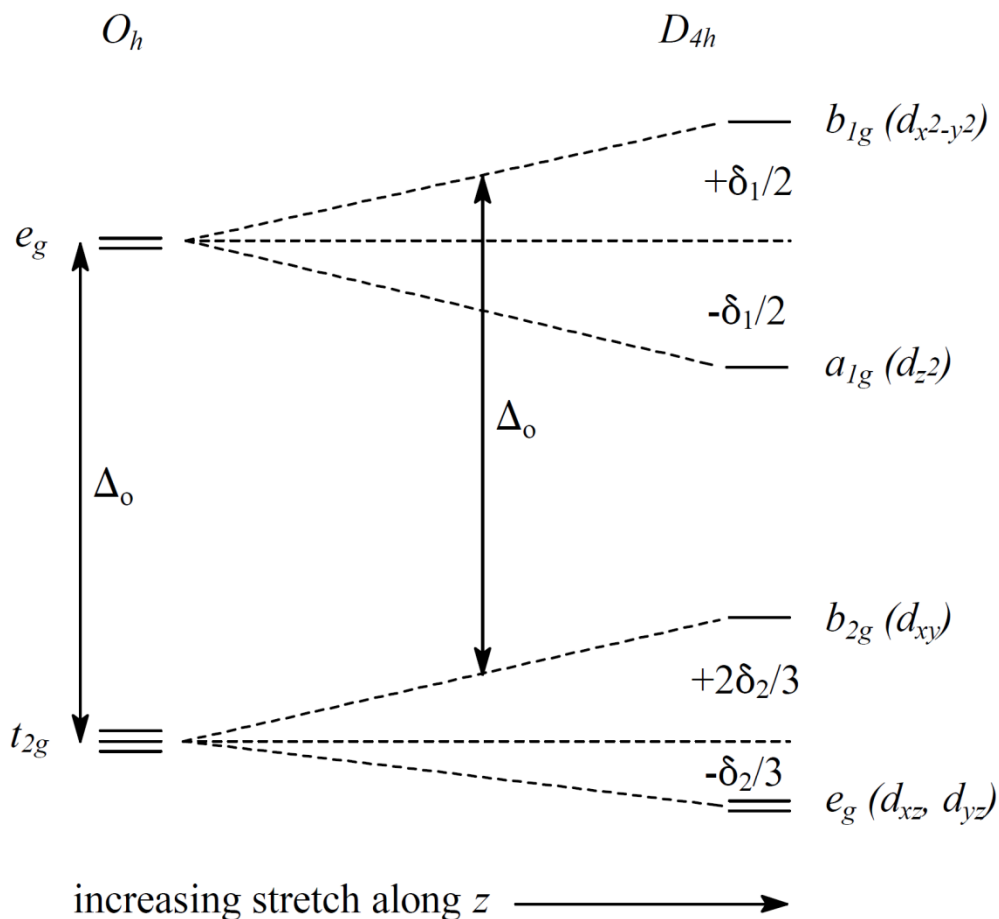
$$e_g = (dxz, dyz)$$



Relative Energies of d orbitals in D_{4h}

- The relative energy ordering of the orbitals depends on the direction and magnitude of the tetragonal distortion.
- A distortion in which the two M-L bonds along z are progressively stretched is an interesting case to consider, because at its limit the two ligands would be removed, resulting in a square planar ML_4 complex.
- Moving the two ligands away from the central metal ion lowers the repulsions between ligand electrons and the metal electrons in d orbitals that have substantial electron distribution along z .
- Thus the energies of the dxz , dyz , and dz^2 orbitals are lowered.
- If we assume that the stretch along z is accompanied by a counterbalancing contraction in the xy plane, so as to maintain the overall energy of the system, then the orbitals with substantial electron distribution in the xy plane will experience increased repulsions.
- Thus, the dxy and dx^2-y^2 orbitals rise in energy.

Orbital splitting from stretching tetragonal distortion



- The upper e_g orbitals of the perfect octahedron split equally by an amount δ_1 , with the dx^2-y^2 orbital (b_{1g} in D_{4h}) rising by $+\delta_1/2$ and the dz^2 orbital (a_{1g} in D_{4h}) falling by $-\delta_1/2$.
- The lower t_{2g} orbitals of the perfect octahedron split by an amount δ_2 , with the d_{xy} orbital (b_{2g} in D_{4h}) rising by $+2\delta_2/3$, and the degenerate dxz and dyz orbitals (e_g in D_{4h}) falling by $-\delta_2/3$.