[Invited Lecture] Theoretical study of electronic structure of transition metal complexes

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Theoretical study of electronic structure of transition metal complexes

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Transition metal complexes

- d shell;

dense lower energy level distribution

electrons in d shell; highly correlating

Theoretical methods

approx. Schroedinger's eq.

counting for electron correlation

applicable to ground and excited states

=> interesting optical, magnetic and various chemical properties

Theory and Program-codes

ab initio technique;

Other than the basic codes of SCF & MCSCF

◎ Development of Multireference Coupled Pair Approximation (MRCPA)

for highly correlating systems

◎ Program Packages of Configuration Interaction (CI);

Alchemy II in this work

characteristics of the methods used

MRCPA ; short range correlation
higher order correlation
size-consistent

Tamm-Dancoff type CI (TDCI);
only long range correlation
(multiple pair correlation)
for predicting a number of excited states
larger system

Multi-reference single and double excitation CI (MRSDCI)
short range correlation
size-inconsistent

If we need a large number of states of rather large system, use of the MRCPA &MRSDCI are not practical.

This method is applied to the 6-nuclear transition metal complexes.

recent results by MRCPA

Electron Affinity of ONiO (extensive basis)

MRSDCI	Davidson type correct'n	MRCPA	obs.
2.44 eV	2.80 eV	3.04 eV	3.05eV

$Mo_2Cl_9^{3-}$	$^1A_1'$	$^3A_2''$(obs.)	$^5A_1'$	$^7A_2''$
cm^{-1}	0.0	772 (~760)	2494	8523
+ $Cr_2Cl_9^{3-}$	(+higher excited states)		=> poster	

Other Poster Presentations

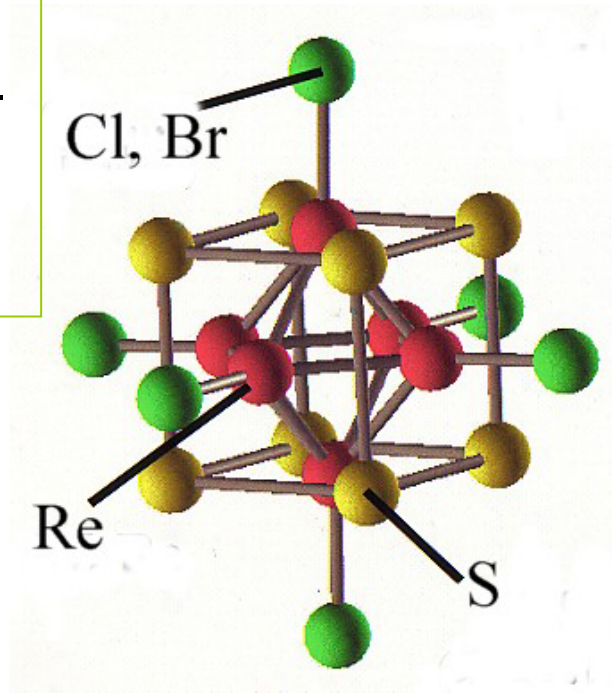
- Theoretical Study on light-induced metastable states in $Na_2[Fe(CN)_5NO]H_2O$

- Electronic Structure of Oxo-Centered Trinuclear Ruthenium Complex

Hexanuclear cluster complex

- $[(Mo_6Cl_8)Cl_6]^{2-}$

- $[(Re_6S_8)Cl_6]^{4-}$, $[(Re_6S_8)Br_6]^{4-}$
- $[(Re_6S_8)Cl_6]^{3-}$



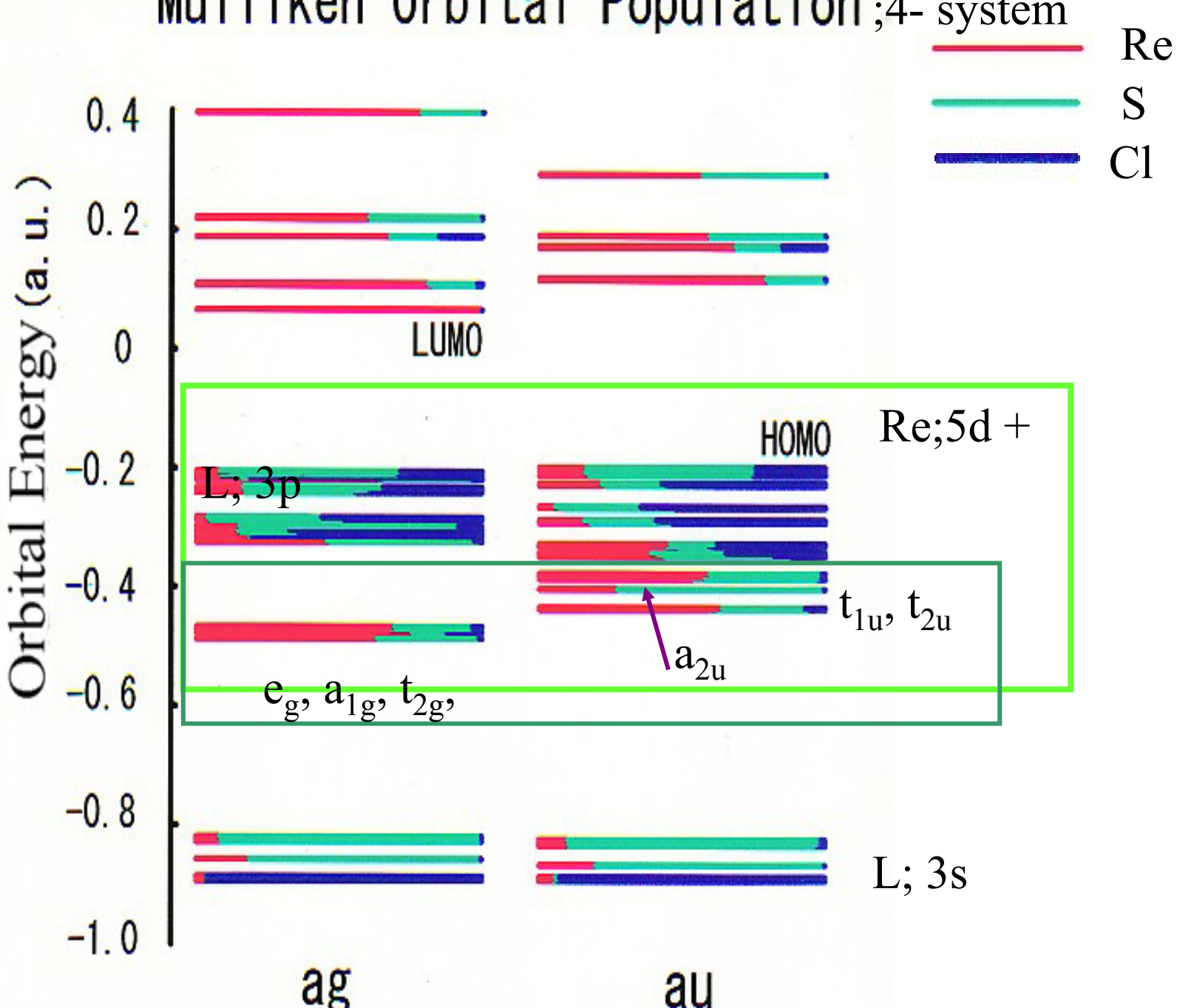
- Electronic structure

- Absorption spectra

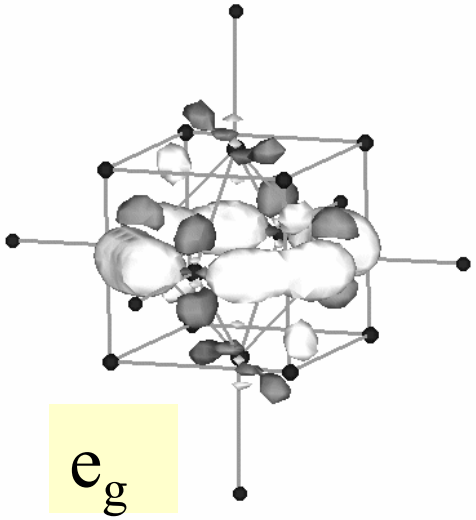
method of calculation

- Relativistic Model Core Potential
- Spin orbit interaction
- Crystal field (the cluster complex embedded in a cage of 728 point charges representing the ionic crystal; Evjen's method)
- Ci symmetry point group

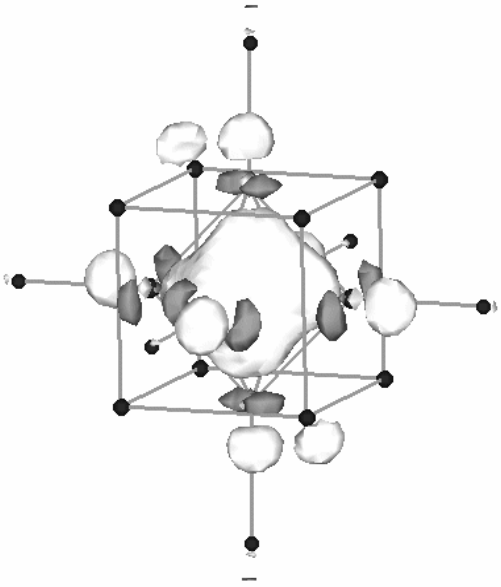
- SCF/TDCI (35 – 80 states)
- (MRSDCI, MRCPA)


Mulliken Orbital Population ;4- system
Re
S
Cl
Orbital Energy (a. u.)
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
LUMO
HOMO
Re;5d +
L; 3p
t_{1u}, t_{2u}
a_{2u}
e_g, a_{1g}, t_{2g},
L; 3s
ag
au

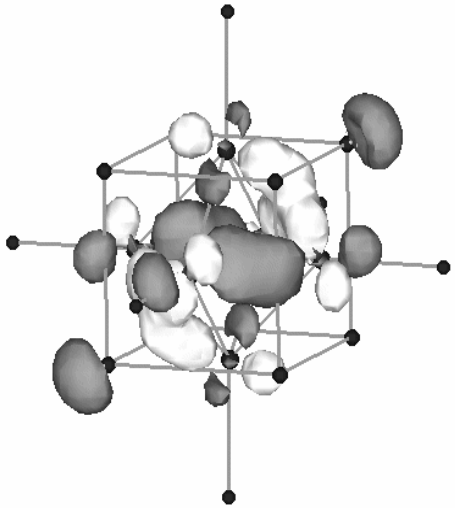
lower d-bonding MO's



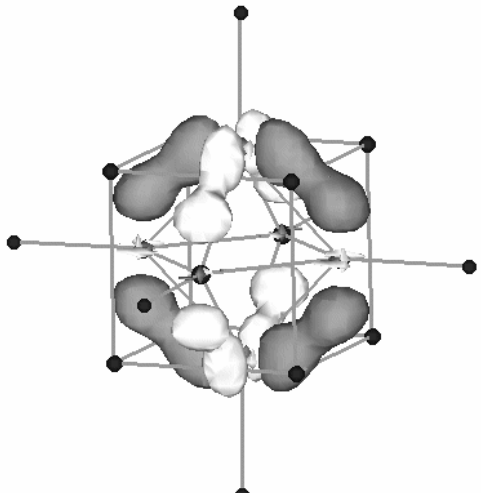
e_g

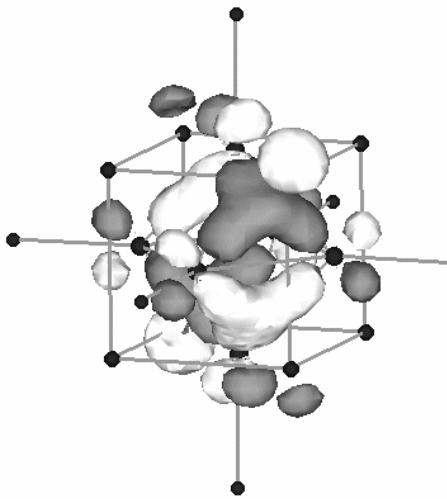


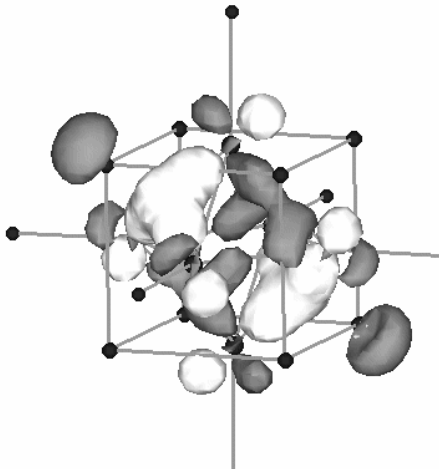
a_{1g}



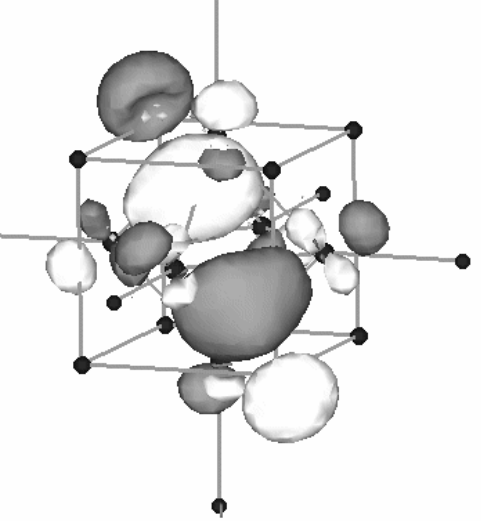
t_{2g}

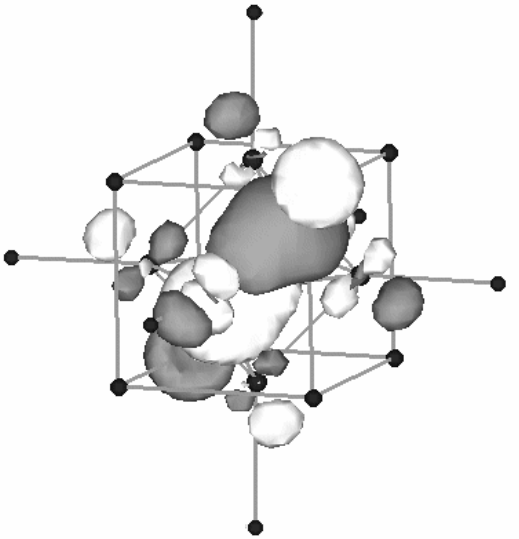


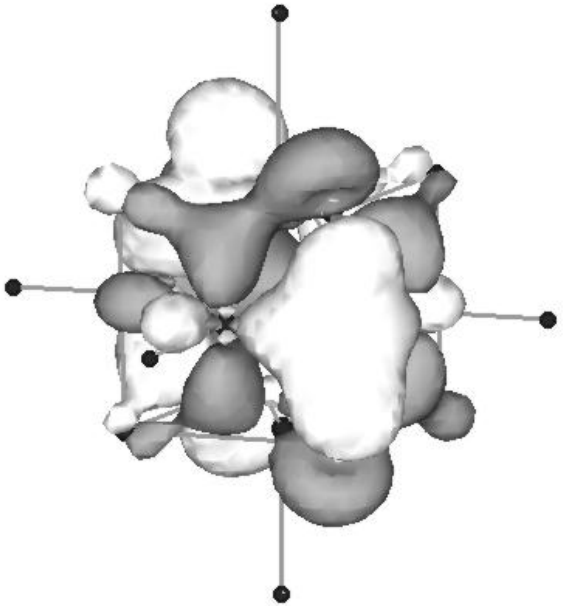




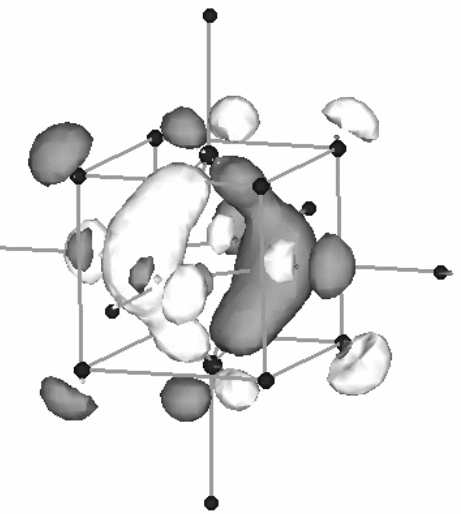
lower d-bonding MOs

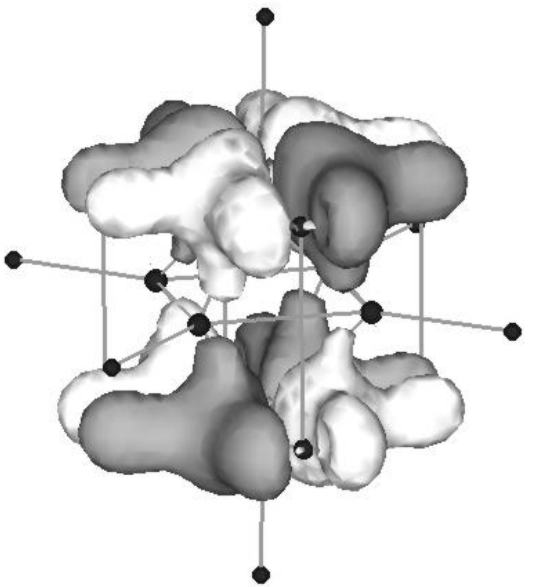




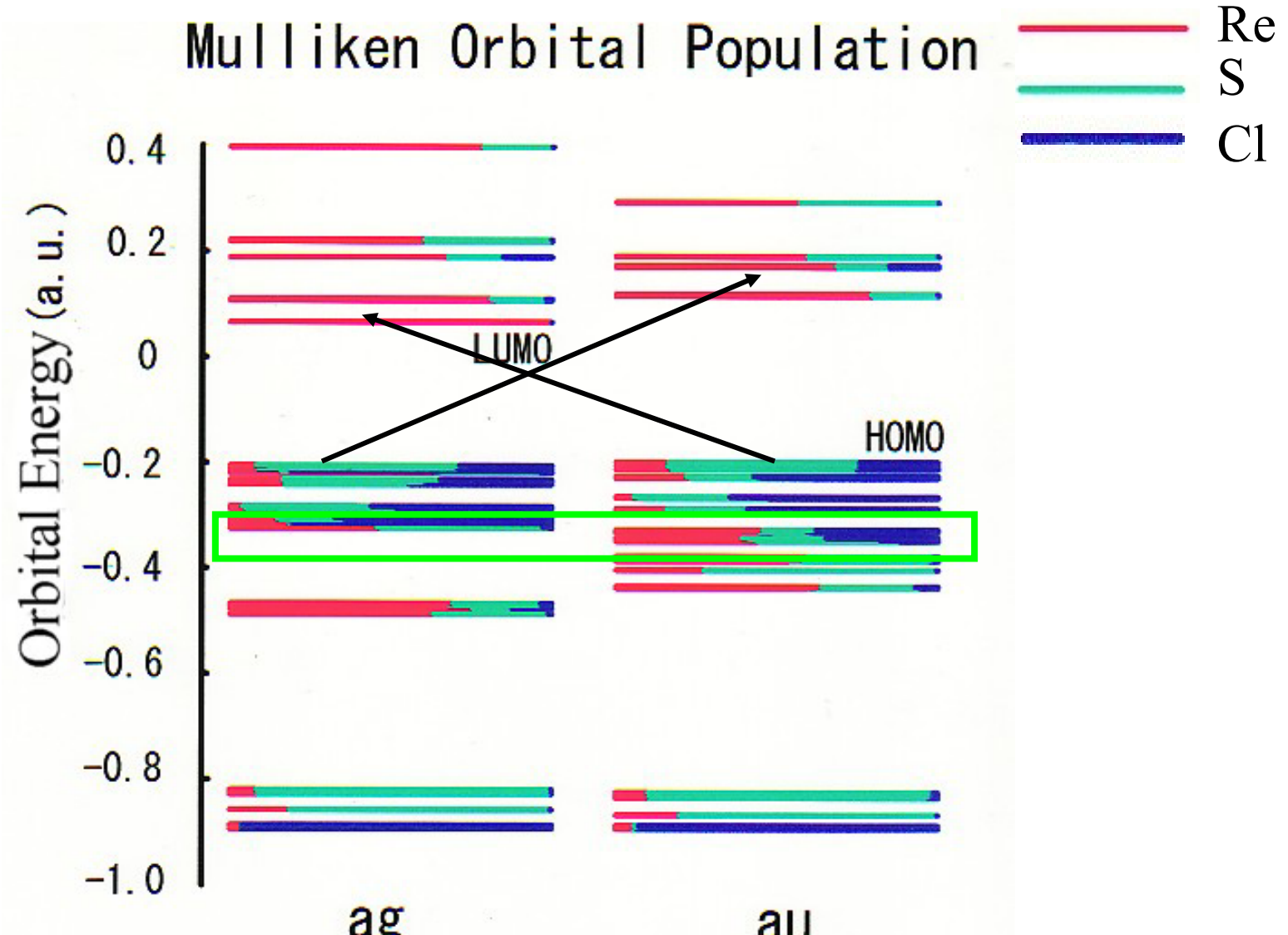


t_{1u}

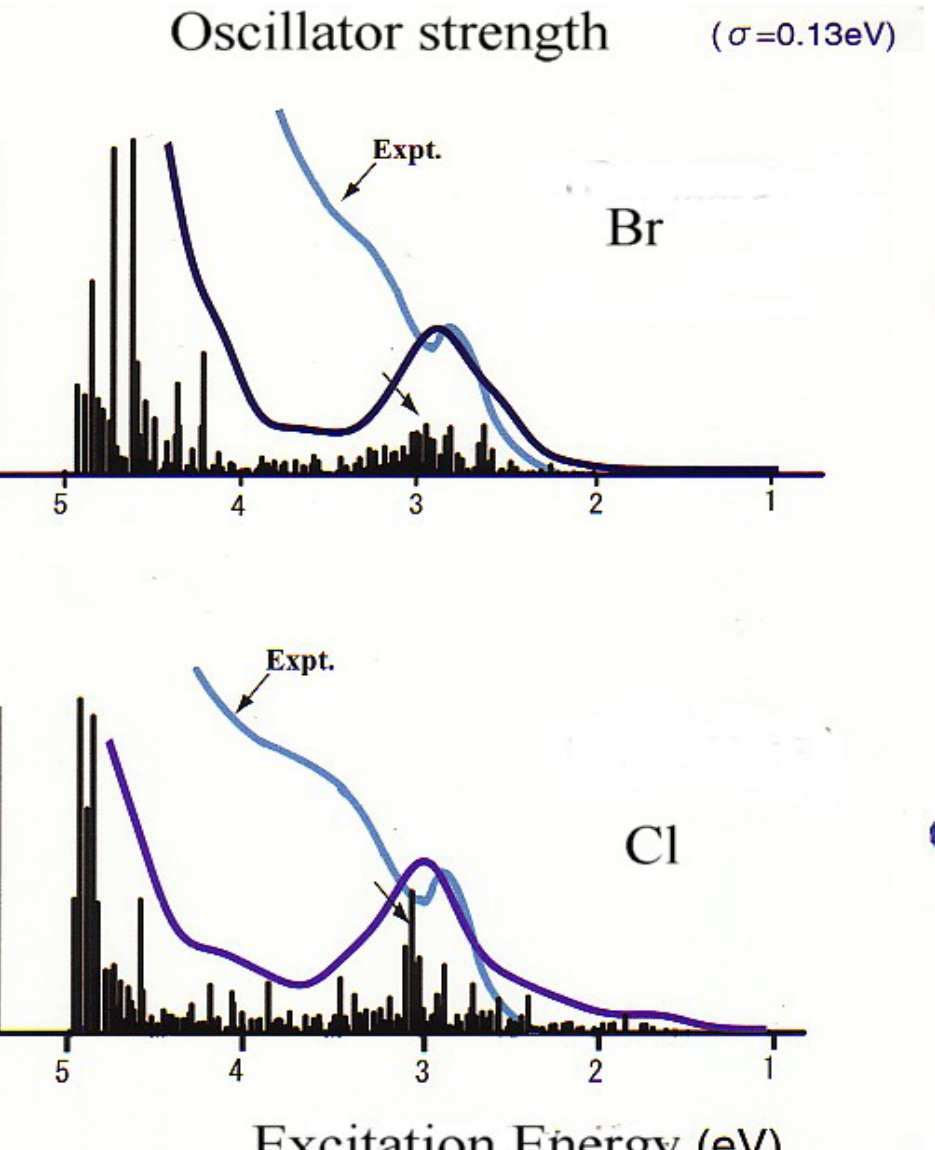


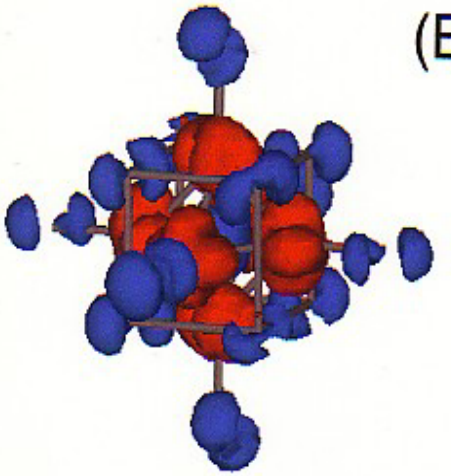


Character of the lower excited states



4- systems; absorption

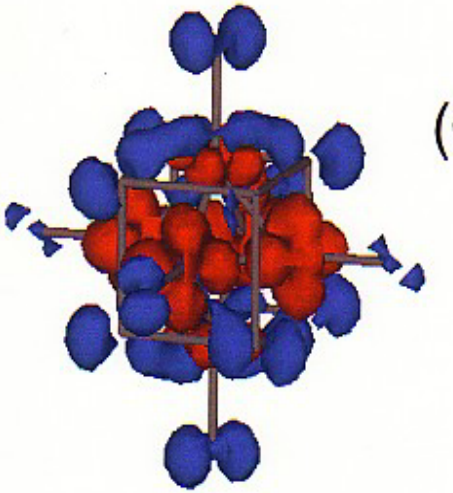




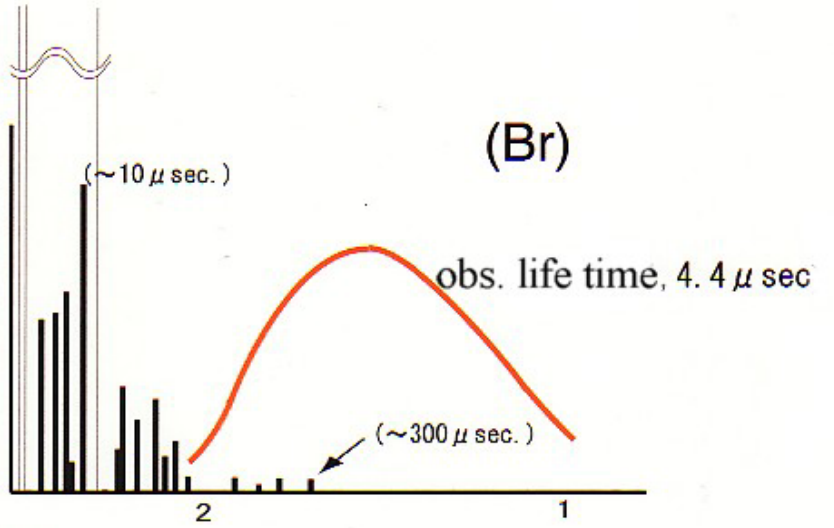
LMCT

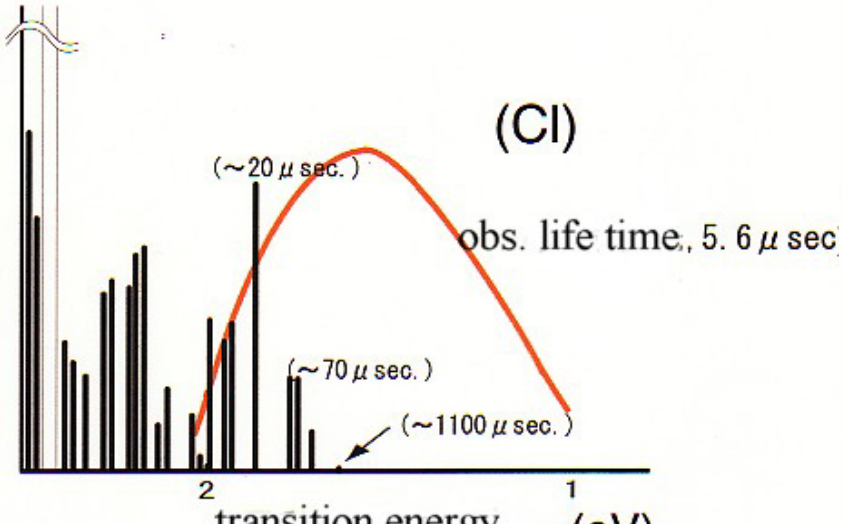
increase

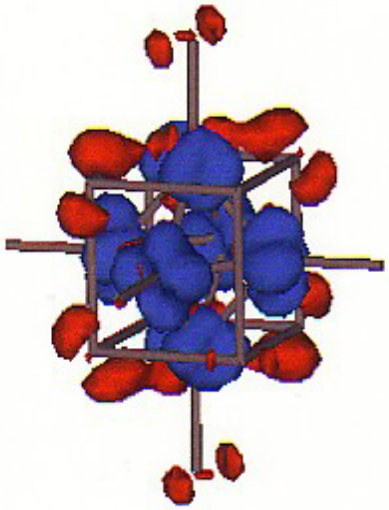
decrease



4- systems; emission



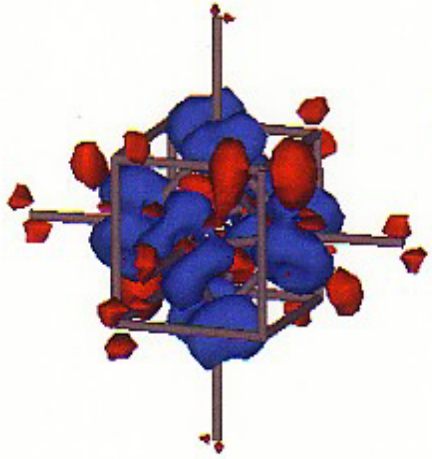




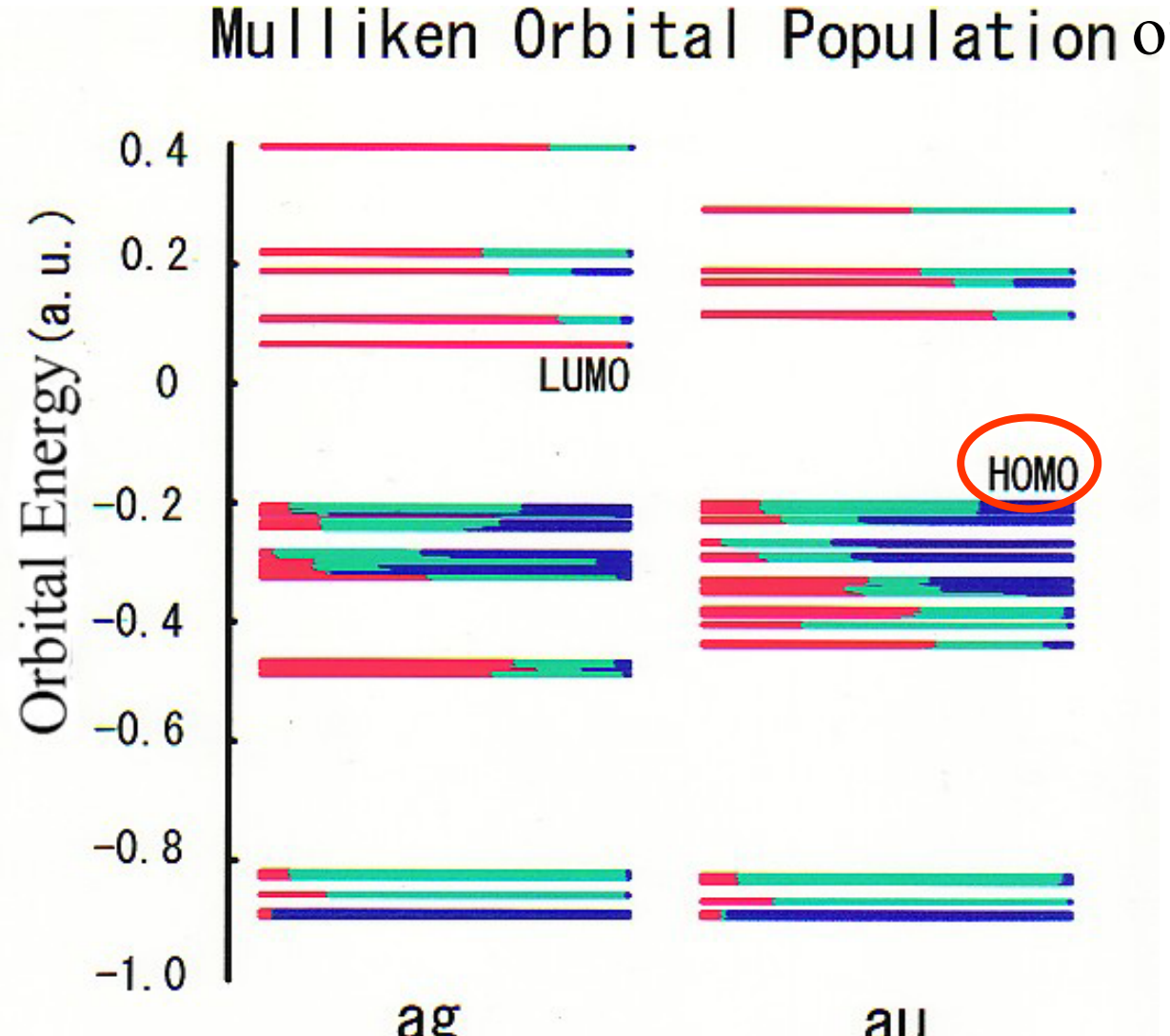
MLCT

increas

decreas

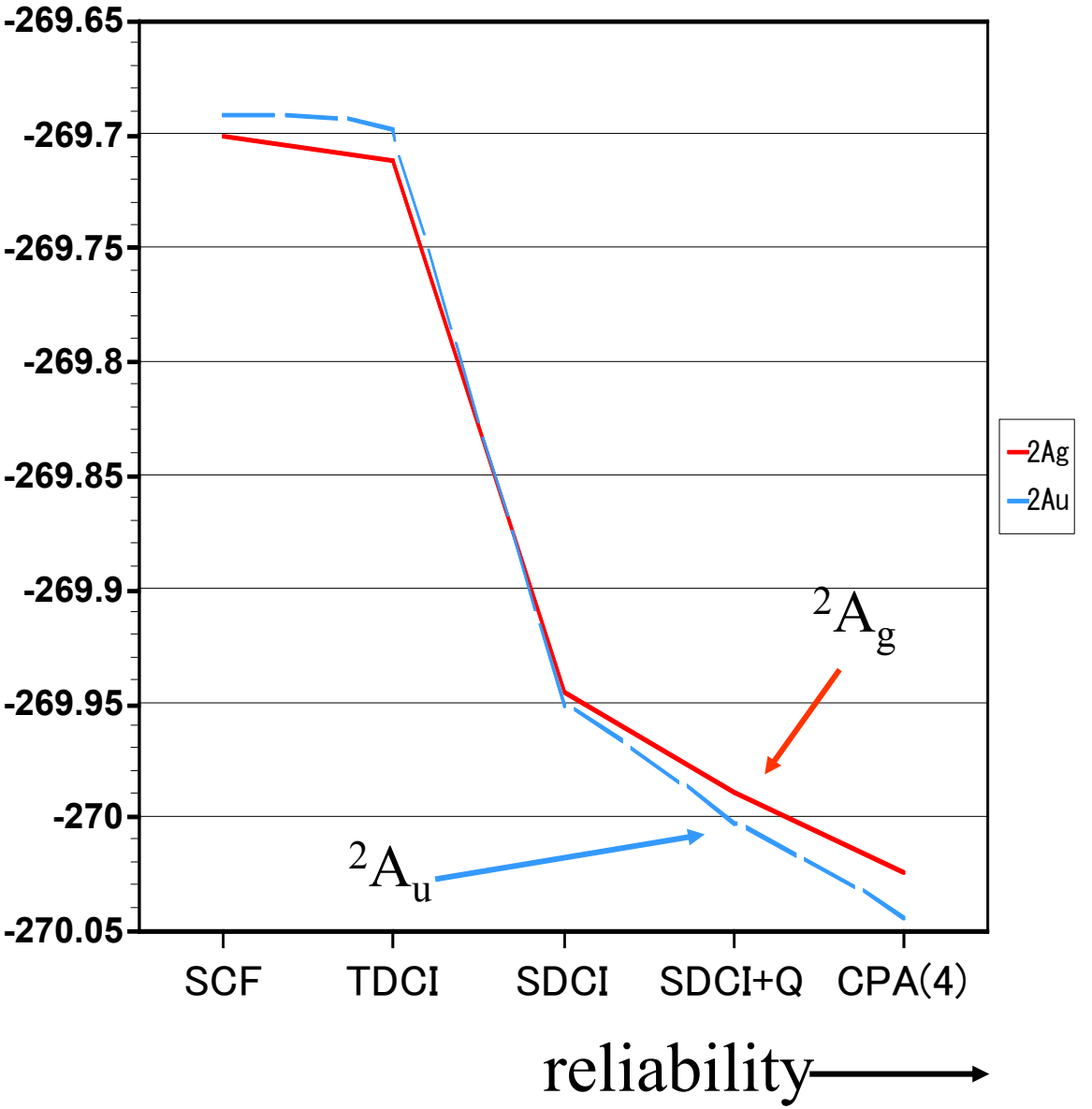


Ground state of 3- system

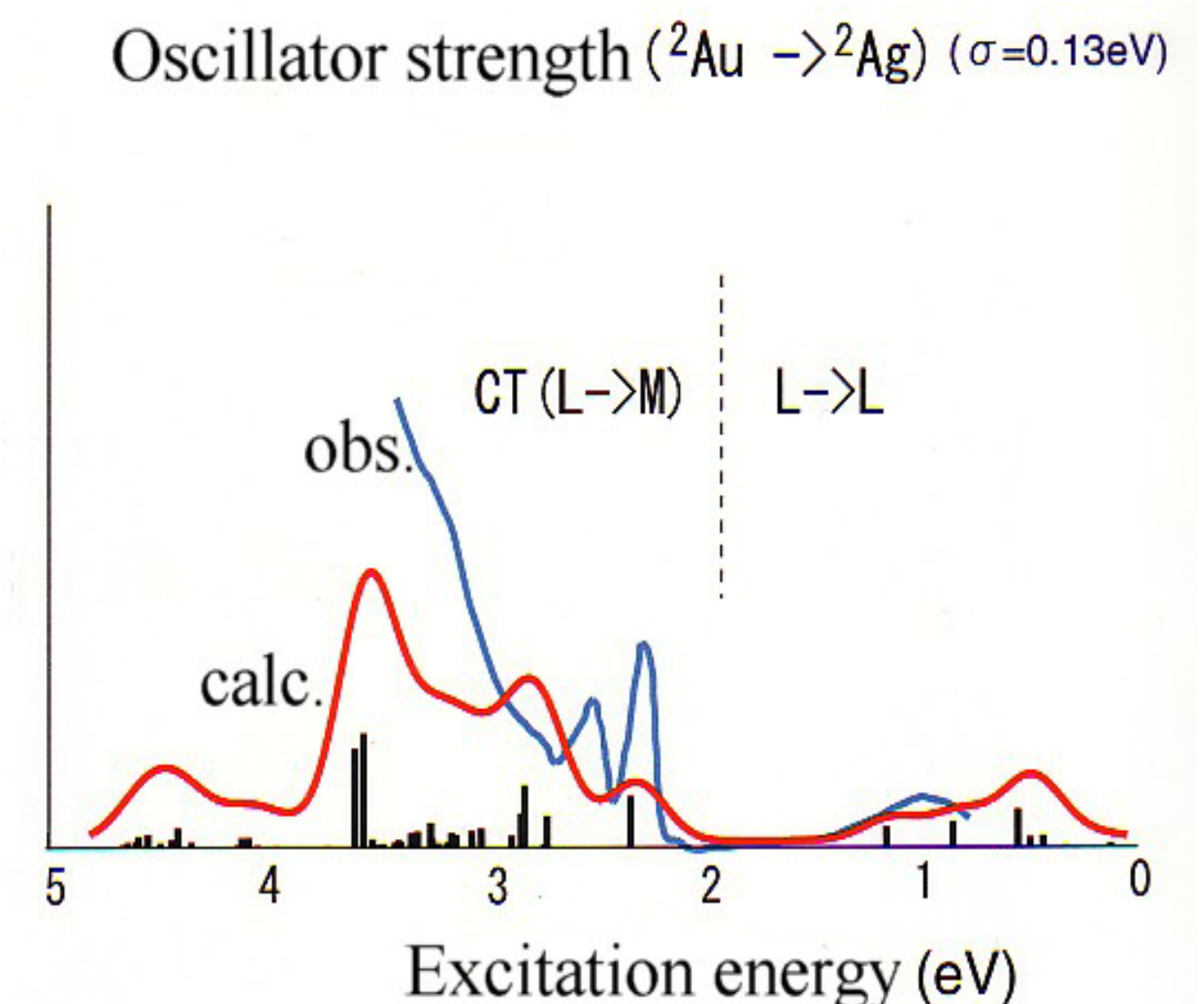


Which is the ground state? ^2A_g or ^2A_u

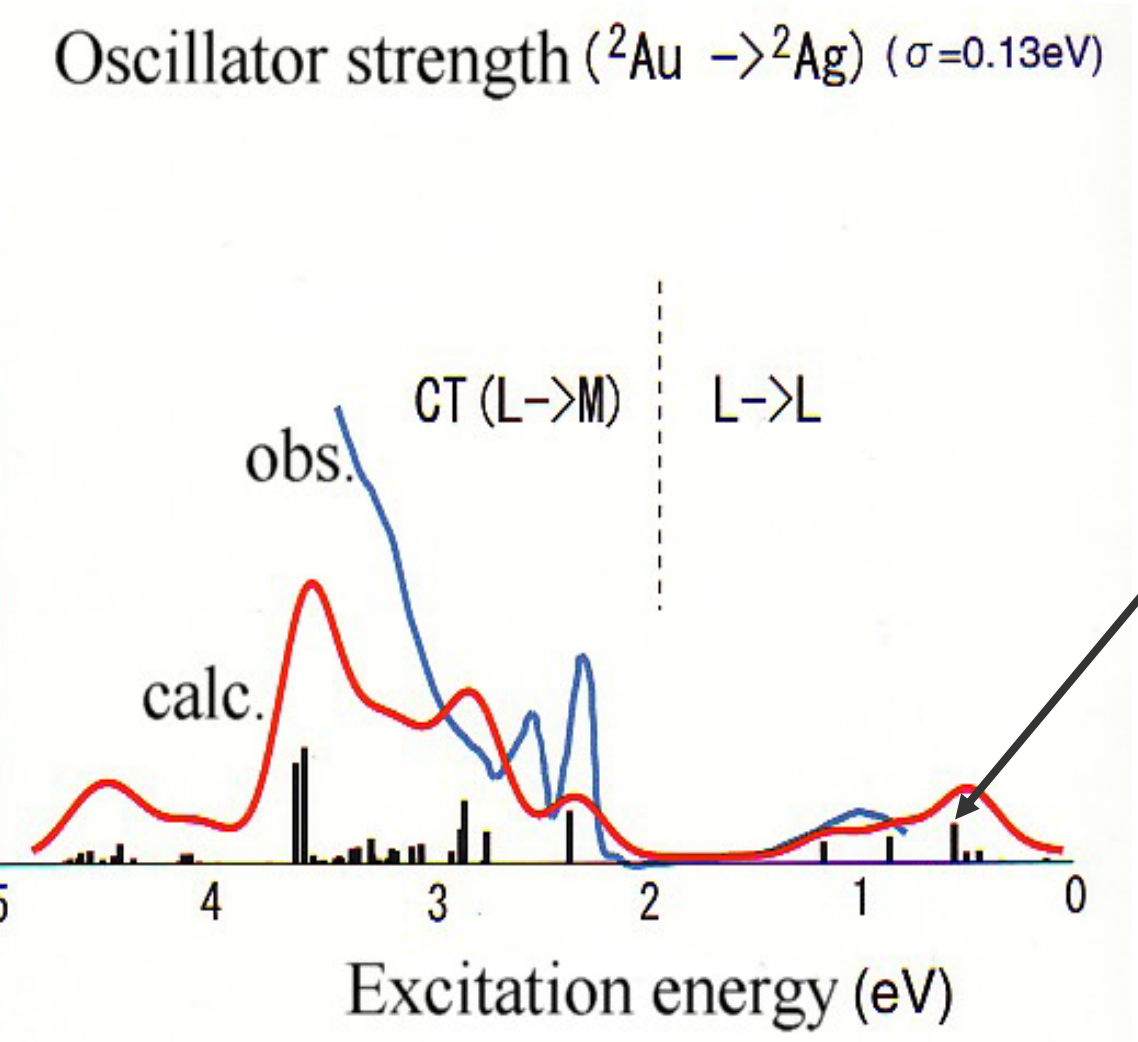
Total energy of the lowest $^2A_{g,u}$ states by several methods

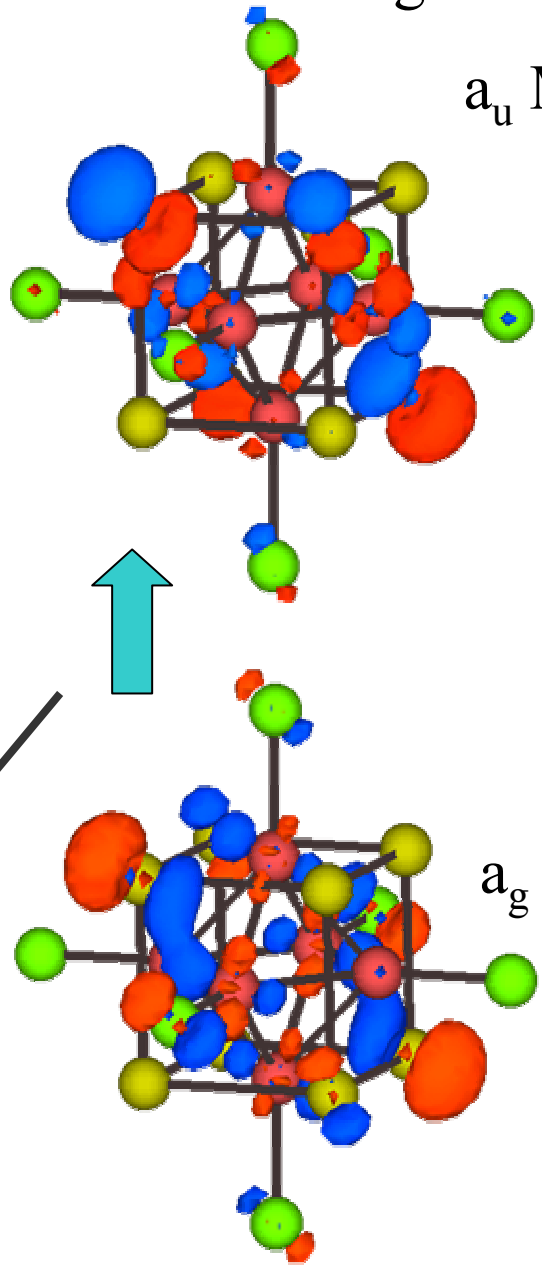


3- system; absorption



half filled in the ground stat





Summary

- Electronic structure of $[(Re_6S_8)Cl_6]^{n-}$ (n=3,4) and $[(Re_6S_8)Br_6]^{4-}$
- Bond : primarily Re-Re + contribution from bridging S
- Higher occupied MO's; large amplitude on ligands
- Lower unoccupied MO's; large amplitude on Re
- Lower excited states of n=4; LMCT
- For n=3, L => L below HOMO-LUMO gap
- Lower state spectra are not strongly dependent on axial ligands (Cl or Br).

Electron Affinity of Halogen atoms & excited state spectra

- F 3.5 eV
- Cl 3.6 eV
- Br 3.4 eV
- I 3.1 eV

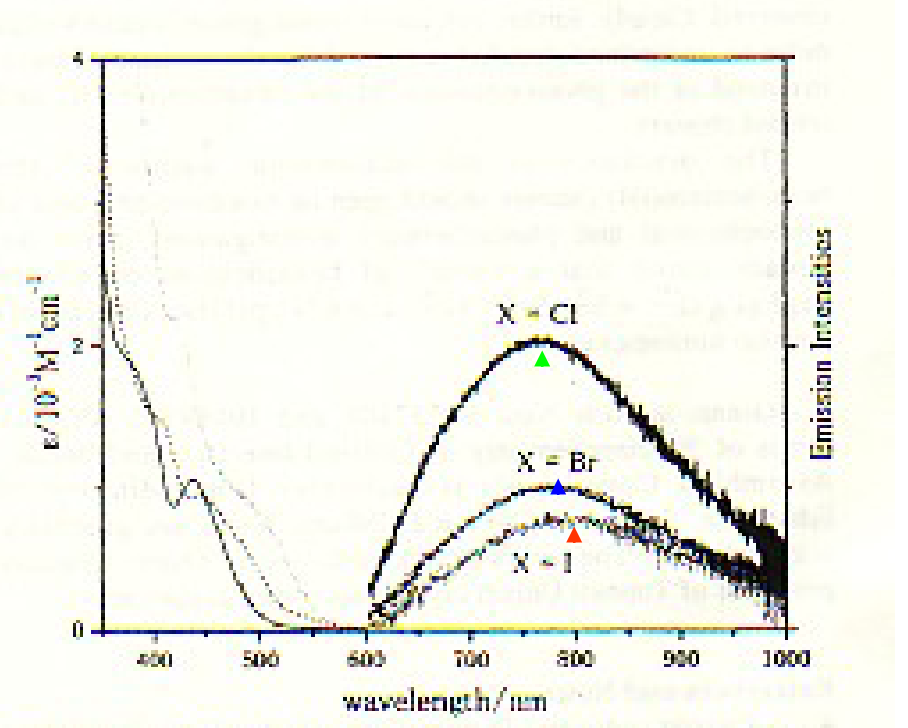
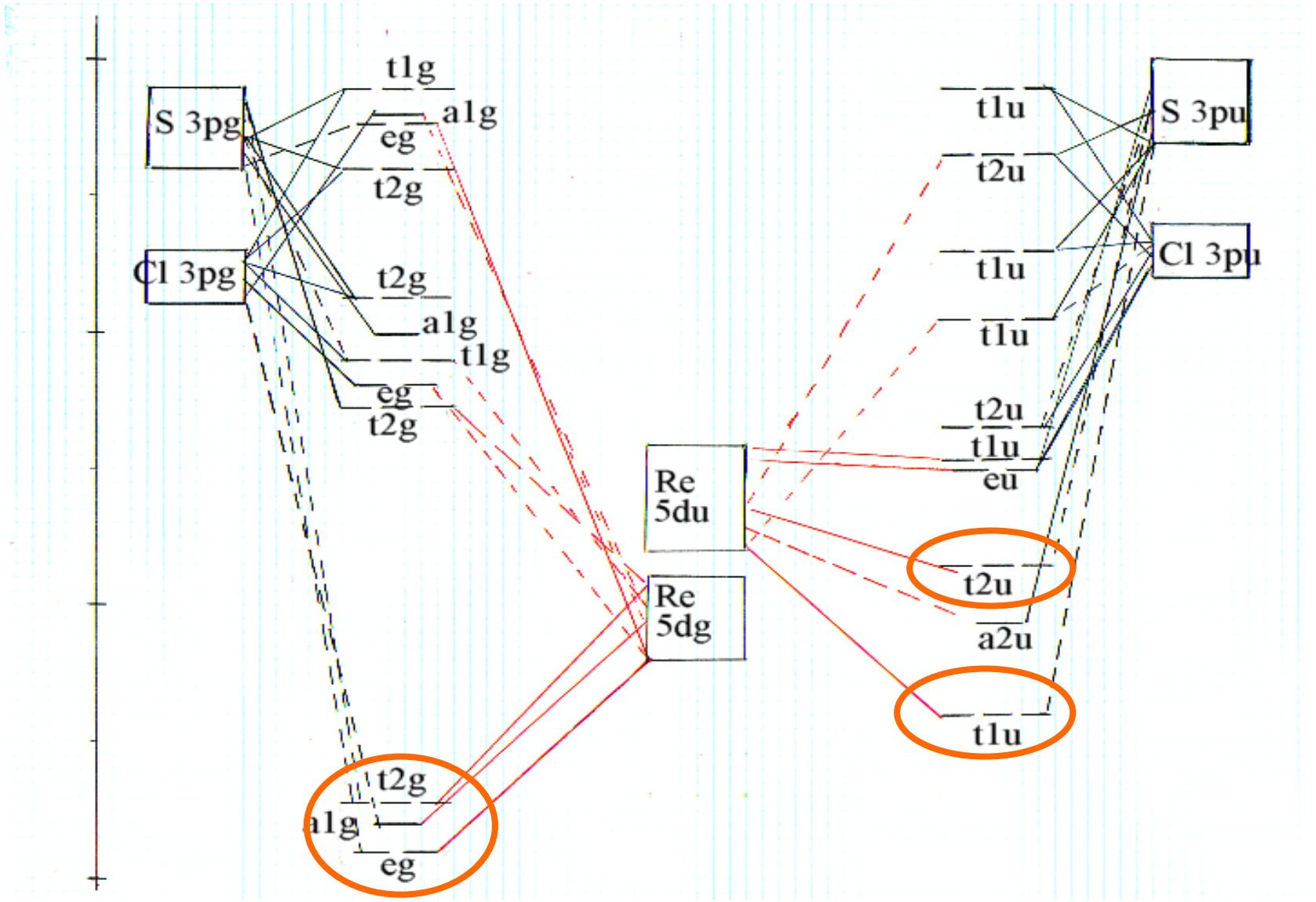
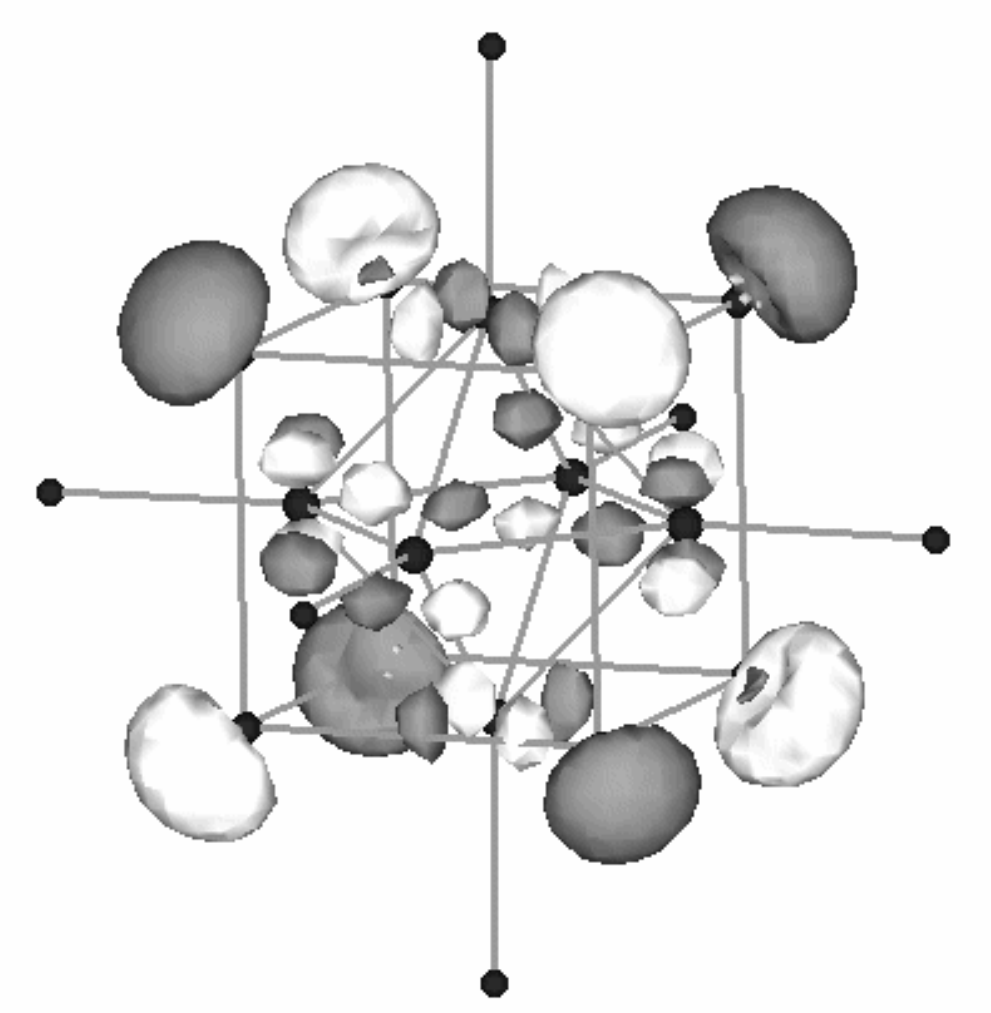


Figure 1. Electronic absorption and emission spectra of (a) $[Re_6S_8Cl_6]^{4-}$ (———), (b) $[Re_6S_8Br_6]^{4-}$ (– – – –) and (c) $[Re_6S_8I_6]^{4-}$ (·····) in acetonitrile.

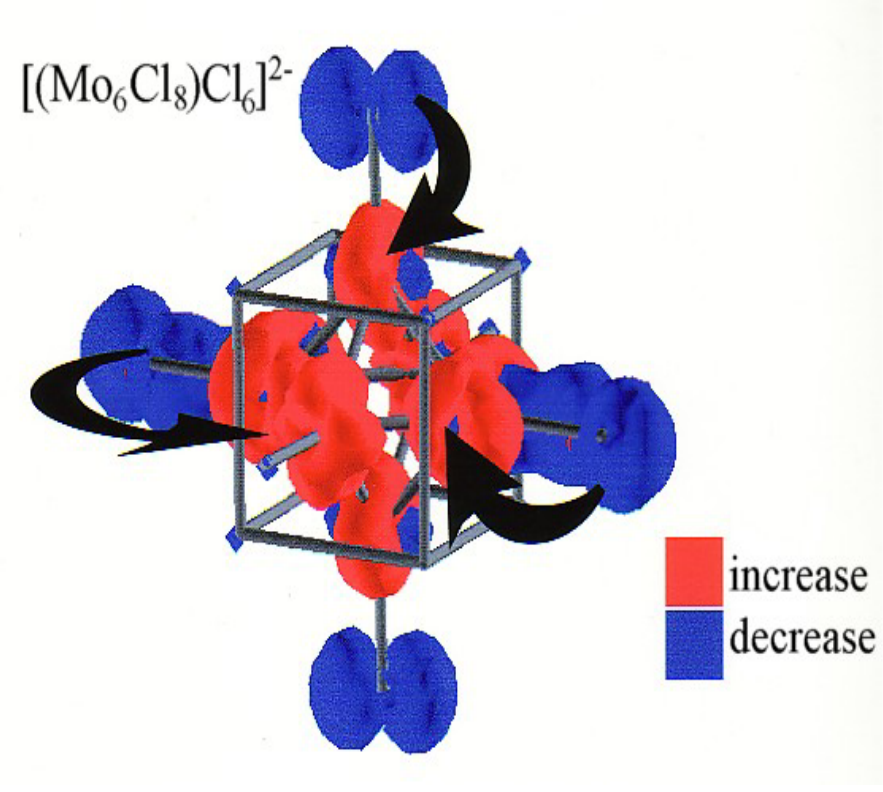
orbital energies (in O_h) ;Re complex

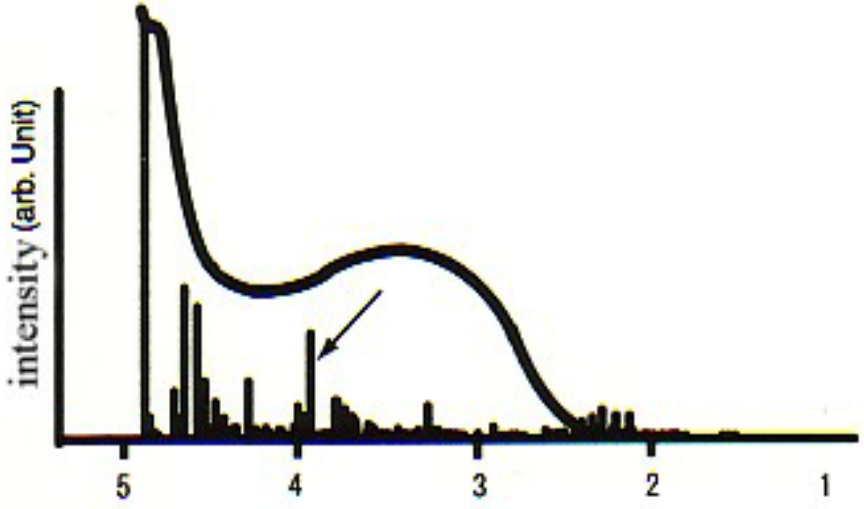


a_{2u} MO

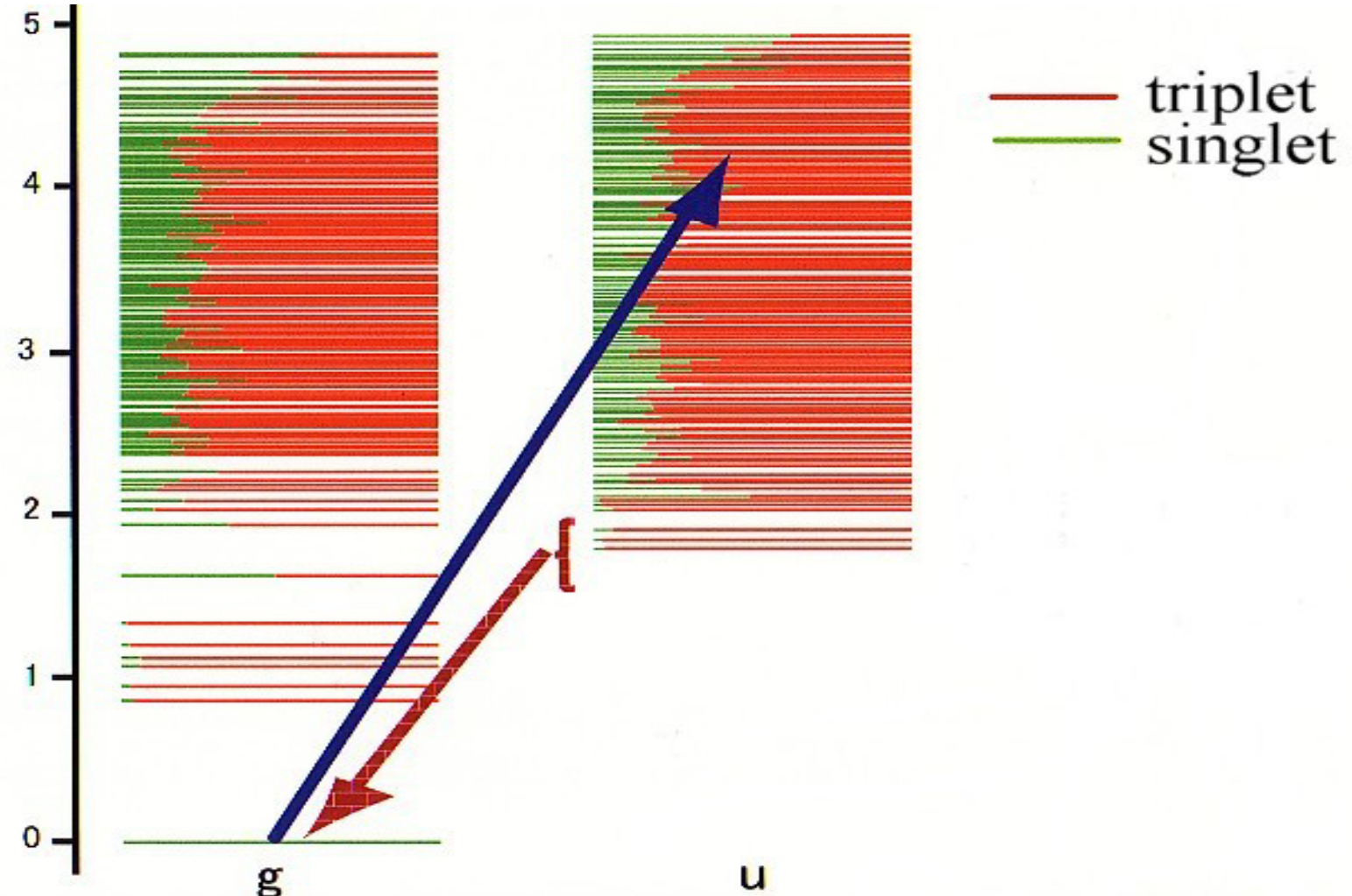


$[(Mo_6Cl_8)Cl_6]^{2-}$

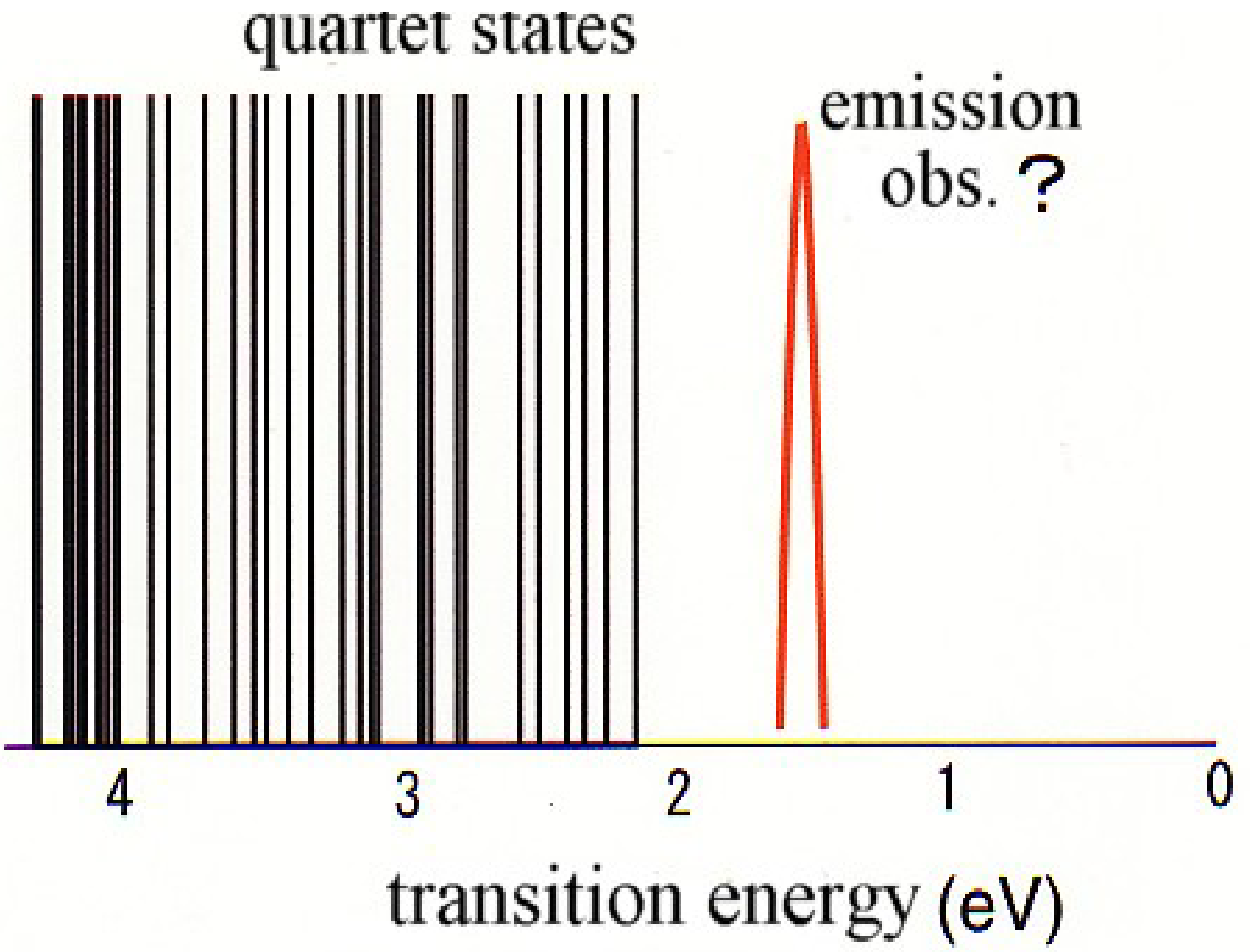




Energetical distribution of the electronic wavefunctions



23 e^- system; emission?



Which is the ground state of the 3- system, ^2A_u or ^2A_g?

	$E(^2A_g)$(a.u.)		$E(^2A_u)$(a.u.)	ΔE(eV)
SCF	-269.6998	<	-269.6904	0.25
TDCI	-269.7114	<	-269.6970	0.39
SDCI	-269.9442	>	-269.9502	-0.18
SDCI+Q	-269.9884	>	-270.0021	-0.37
CPA(4)	-270.0237	>	-270.0436	-0.54

$\Delta E = E(^2A_g) - E(^2A_u)$

Bonding Characteristics

- d-d bonding
- + supporting bridging ligands
- + surrounding ligands

Performance

- TDCI MRSDCI MRCPA
- Accuracy $<$ $<$
- Storage & time $<$ $\lesssim$