

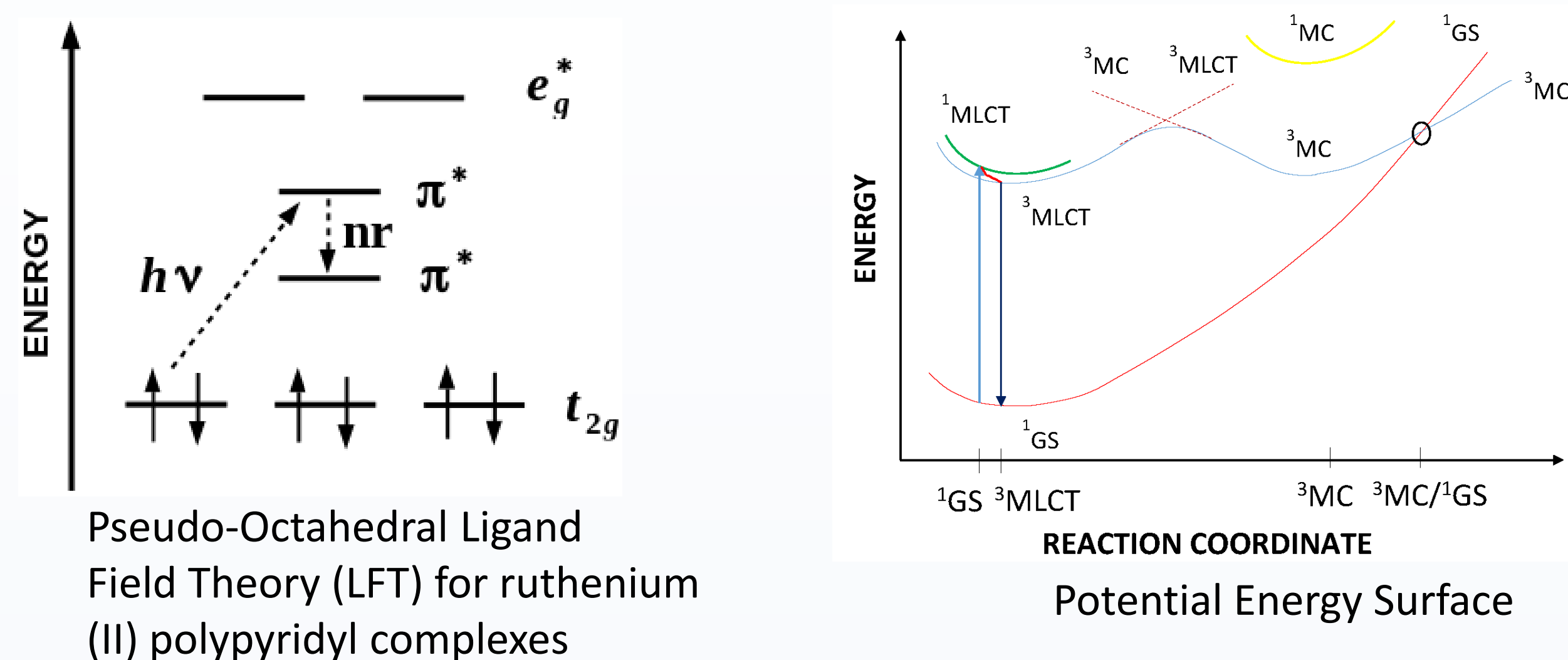
Test of the Orbital-Based LI3 Index as a Predictor of the Height of the $^3\text{MLCT} \rightarrow ^3\text{MC}$ Transition-State Barrier for Gas-Phase $[\text{Ru}(\text{N}\wedge\text{N})_3]^{2+}$ Polypyridine Complexes

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INTRODUCTION

This work concerns the luminescence lifetimes of Ru(II) polypyridine complexes such as the much studied tris(2,2' bipyridine) ruthenium(II) ion. The present work is part of the continuation of previous work aimed at clarifying factors responsible for long luminescence lifetimes which has already resulted in two publications [1, 2]. These two publications sought to find ligand field theory (LFT) like luminescence indices which correlated with experimental high luminescence lifetimes. A more direct evaluation of the luminescence indices involves calculating the height of the transition state barrier (or barriers) on the lowest triplet state potential energy surface of these complexes. It is the goal of the present study to calculate these barriers for at least several of these complexes to compare against the previously developed luminescence indices.



The difference between the $^3\text{MLCT}$ and ^3MC states is whether the excited electron is in a ligand π^* orbital or in a metal e_g^* orbital.

Relative positions of the metal t_{2g} and e_g^* energies and the ligand π^* energies can predict the $^3\text{MLCT} \rightarrow ^3\text{MC}$ barrier height.

OBJECTIVES

$$LI3 = \frac{\left[(\epsilon_{e_g^*} + \epsilon_{\pi^*}) / 2 \right]^2}{(\epsilon_{e_g^*} - \epsilon_{\pi^*})}$$

Direct calculation of the $^3\text{MLCT} \rightarrow ^3\text{MC}$ barriers (E^\ddagger) at the same level as LI3 (gas-phase calculations, B3LYP/6-31G, 6-31G(d)).

SPECIAL TOOLS

SPECTRUM.PY: Converts the spectral function to the molar extinction coefficient for comparison against experiment.

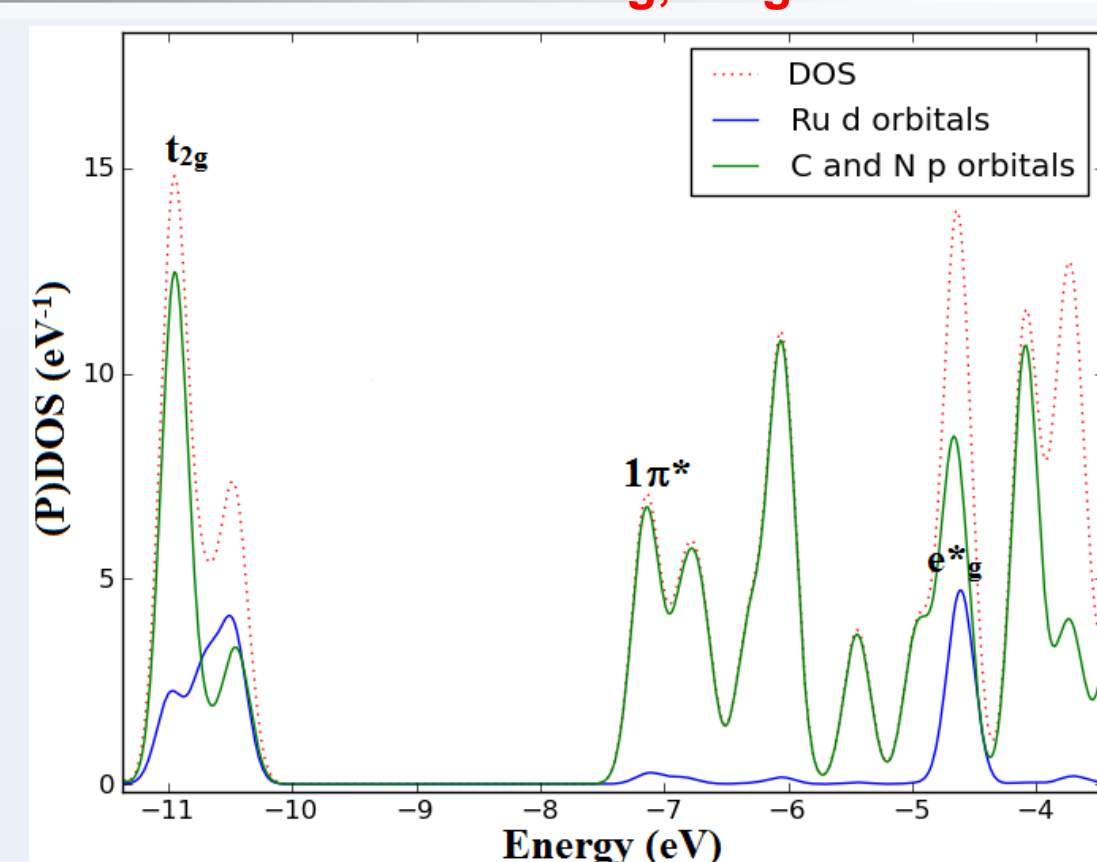
$$S(\omega) = \sum_I f_I \delta(\omega - \omega_I) \quad \text{to} \quad \epsilon(\omega) = \frac{\pi N_A e^2}{2 \epsilon_0 m_e c \ln(10)} S(\omega)$$

PDOS.PY: PDOS analysis based upon Mulliken charges technique to extract ligand field theory (LFT) like information from DFT calculations.

COMPUTATIONAL DETAILS

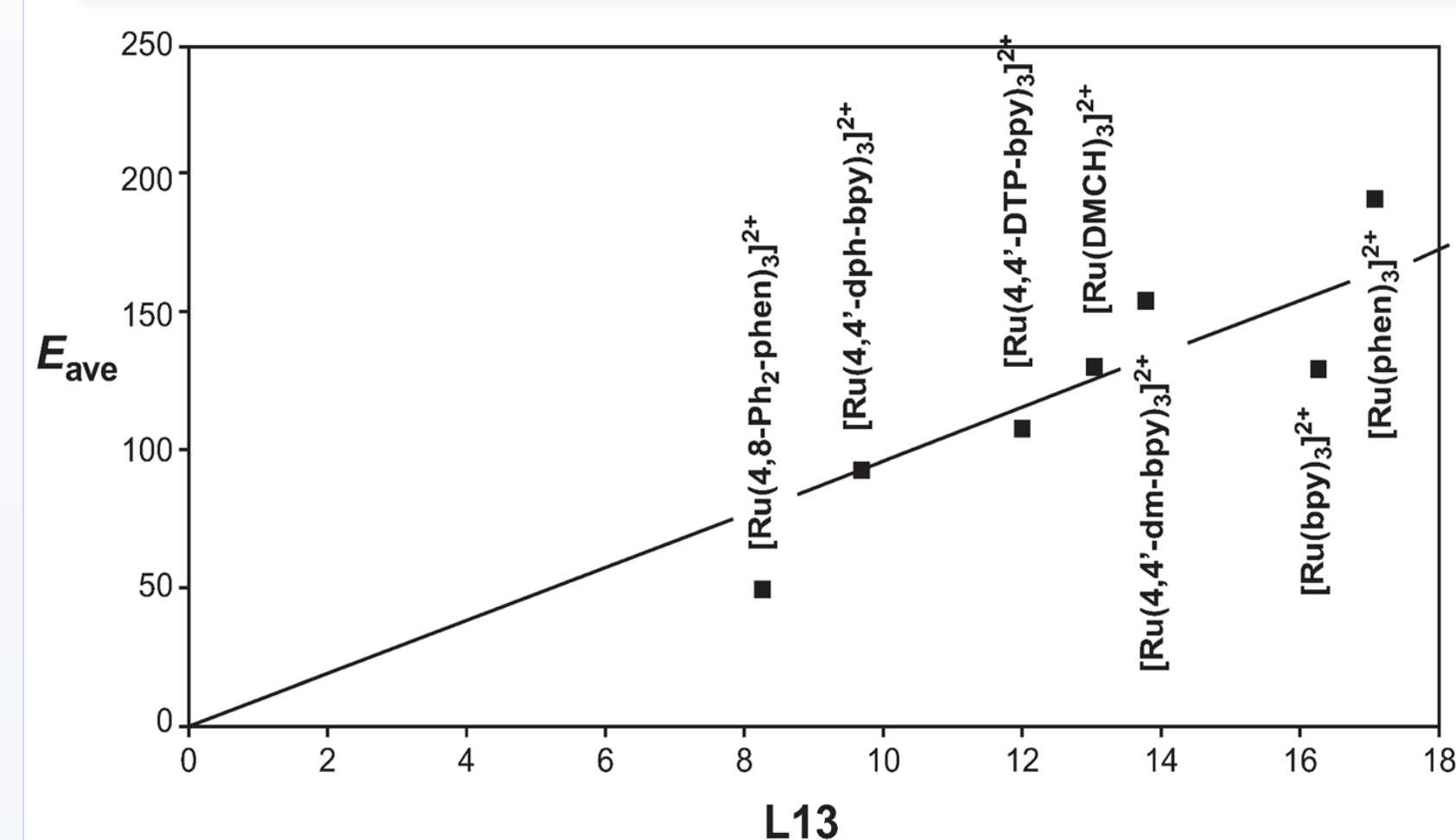
- GAUSSIAN 09, B3LYP/6-31G and 6-31G(d) LANL2DZ EC for Ru. Ultrafine grid and Very Tight SCF, DFT, TD-DFT, IRC
- ORCA, NORI, B3LYP/G, NEB
- Trans-dissociation of two bonds (2D-scan) with a step size of 0.005 is done from 1.90 to 2.50 Å to find a possible 3TS.

EXTRACTION OF t_{2g} , e_g^* , AND π^* ENERGIES FROM PDOS-LFT



B3LYP (P)DOS calculated for $[\text{Ru}(\text{bpy})_2(4,7\text{-Ph}_2\text{-phen})]^{2+}$ for 6-31G basis set

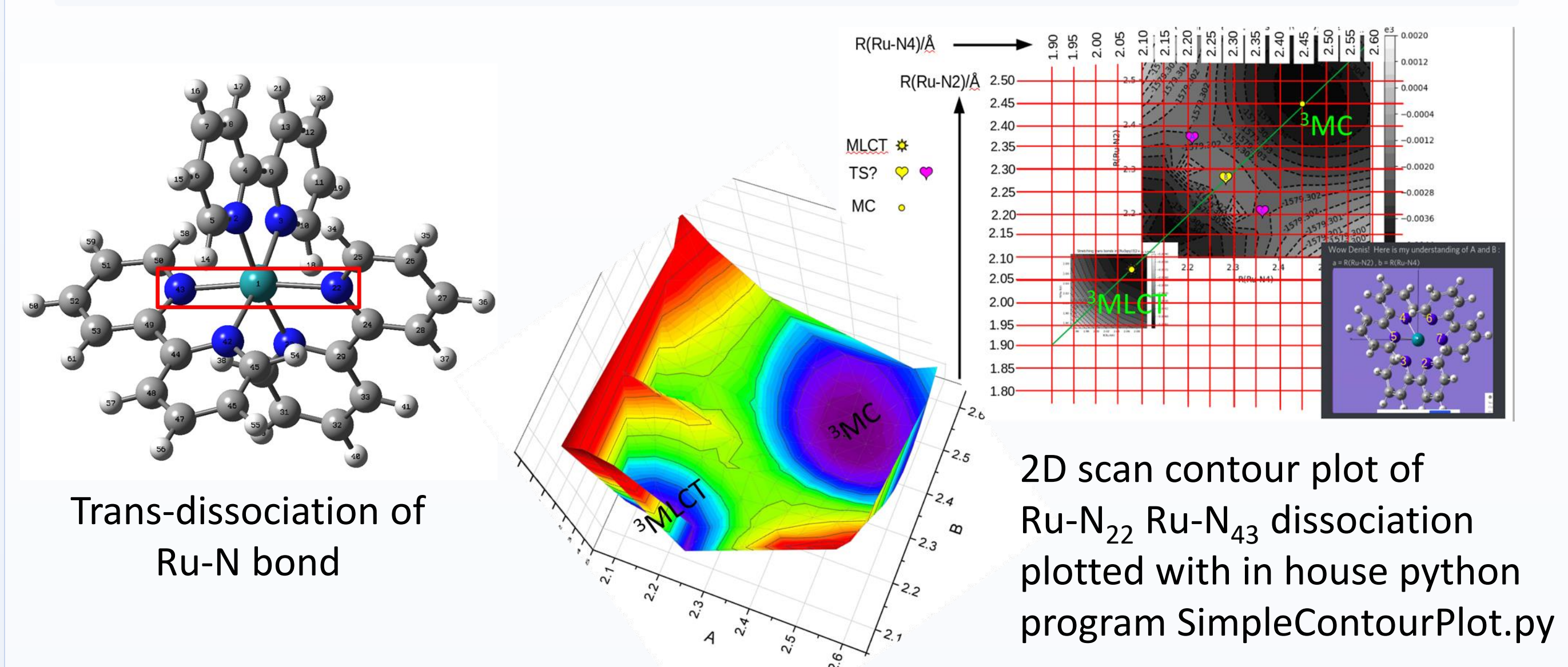
PERFORMANCE OF LI3



Performance of LI3 for complexes of formula $[\text{RuX}_3]^{2+}$. LI3 is in (eV)

E_{ave} is not the true $^3\text{MLCT} \rightarrow ^3\text{MC}$ barrier height but rather an indicative value deduced from lifetimes of the complexes at 298 and 77 K. Need to calculate size of triplet barrier theoretically so as to fit in LI3 for the complexes in the graph.

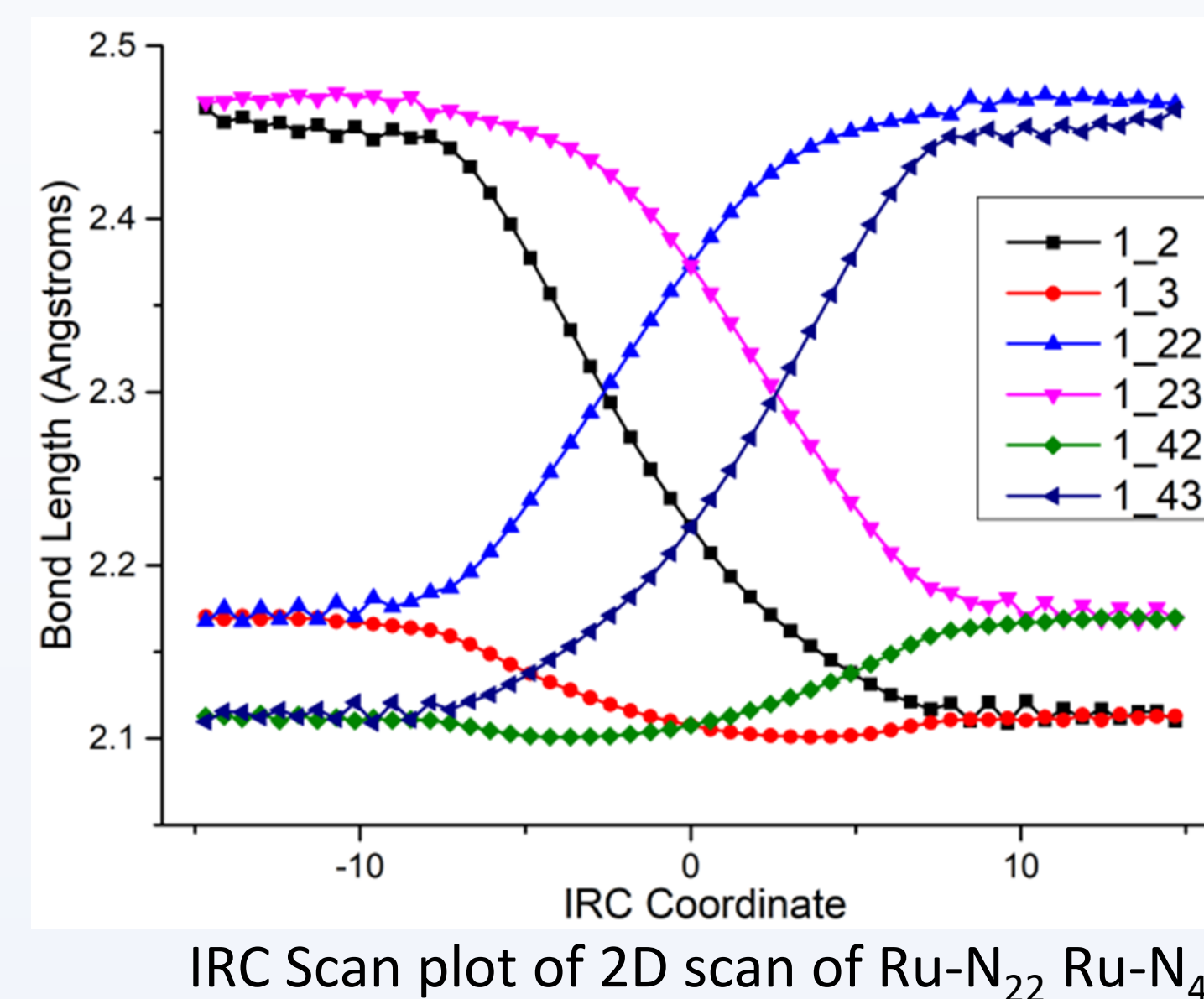
2D SCAN CONTOUR PLOT



Trans-dissociation of Ru-N bond

2D scan contour plot of Ru-N₂₂-Ru-N₄₃ dissociation plotted with in house python program SimpleContourPlot.py

BOND LENGTH VARIATION WITH IRC SCAN



- There is overly large symmetry of the IRC and associated Ru-N distance plot.
- "Pseudorotation" ^3TS point between ^3MC Jahn-Teller distorted structures detected which is close to expected TS.
- Use an alternative algorithm for finding the IRC is by using the nudged elastic band (NEB) method.

CONCLUSION

- New difficulties were encountered in the project due, apparently, to near-lying transition states or to transition states shared by more than one reaction pathway.
- We have developed many techniques, and overcome many difficulties, for finding and proving TSs in ruthenium polypyridine complexes.
- New Nudged Elastic Band (NEB) calculations started with the ORCA program with NORI, B3LYP/G to get a better/more accurate guess for the ^3TS .

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