

Computational Investigation into the Nature of Technetium-Technetium Bonding Within the Octachloroditechnetate ($\text{Tc}_2\text{Cl}_8^{2-/3-}$) Anions

Johnson Liu, Anthony Dutoi

Overview

Molecules involve groups of atoms held together through the interaction between the atoms' electrons. The behavior of these electrons can be represented by wave functions which contain information about each electrons' position and motion. Each atom's wave function describes a set of atomic orbitals, each with certain energy levels, in which the atom's electrons can be located. When atoms interact with each other, the atoms' electrons are shared amongst each of the participating atoms and a new wave function arises, corresponding to a new set of molecular orbitals. The molecular orbitals of the new molecule represent the locations in which the shared electrons can be located.

The model of bond order provides a qualitative relationship between the bond order and the length of a bond between two atoms. An increase in bond order accompanies a decrease in bond length. Likewise, a decrease in bond order corresponds to an increase in bond length. However, a case that deviates from this expected trend has been found in the literature.¹ In the case of the octachloroditechnetate ($\text{Tc}_2\text{Cl}_8^{2-/3-}$) anions, as bond order increases between the two technetium (Tc) atoms, the bond length between the atoms also increases, contrary to the expected outcome. Figure 1 shows the expected trend in Tc-Tc bond length between the two $\text{Tc}_2\text{Cl}_8^{2-/3-}$ anions and the experimental and theoretical Tc-Tc bond lengths found in the literature. Other theoretical results from the literature are inconclusive on the relationship between bond order and bond length for the Tc-Tc bond.² Different functionals were used to calculate for the Tc-Tc bond length. Figure 2 shows the difference in Tc-Tc bond length between the $\text{Tc}_2\text{Cl}_8^{2-/3-}$ anions as calculated by the various functionals. Only one of the functionals, BHHLYP, was able to reproduce the experiment trend.

The authors of the experimental study calculated the bond order of these anions under the assumption that the conventional view of bond order adequately accounts for the behavior of the bonding that occurs within the $\text{Tc}_2\text{Cl}_8^{2-/3-}$ anions. It should be noted that the concept of bond order represents a very basic approximation of the nature of bonding between atoms. This view assumes that each molecular orbital can have exactly zero, one, or two electrons and that each bonding or antibonding orbital contributes equally to the bonding or the antibonding, respectively, between atoms within a molecule. However, each orbital can contribute to the bonding or antibonding between atoms to varying degrees. Also, certain molecular orbitals can have no effect on the bonding or antibonding between two atoms and thus behave as nonbonding orbitals.

In this study, geometry optimization calculations were carried out on the $\text{Tc}_2\text{Cl}_8^{2-/3-}$ anions using different combinations of functionals and basis sets/effective core potentials (ecps) in order to determine the Tc-Tc bond length as predicted by each of the combinations. The Tc-Tc bond distance in which the anion has the lowest energy should be the most stable Tc-Tc bond length.

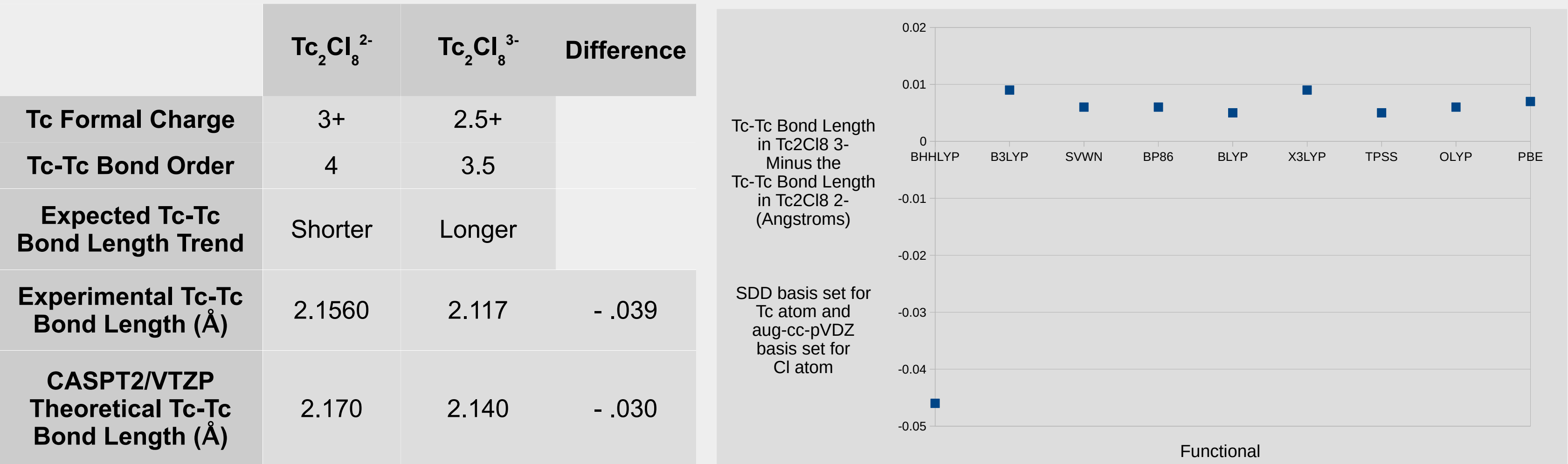
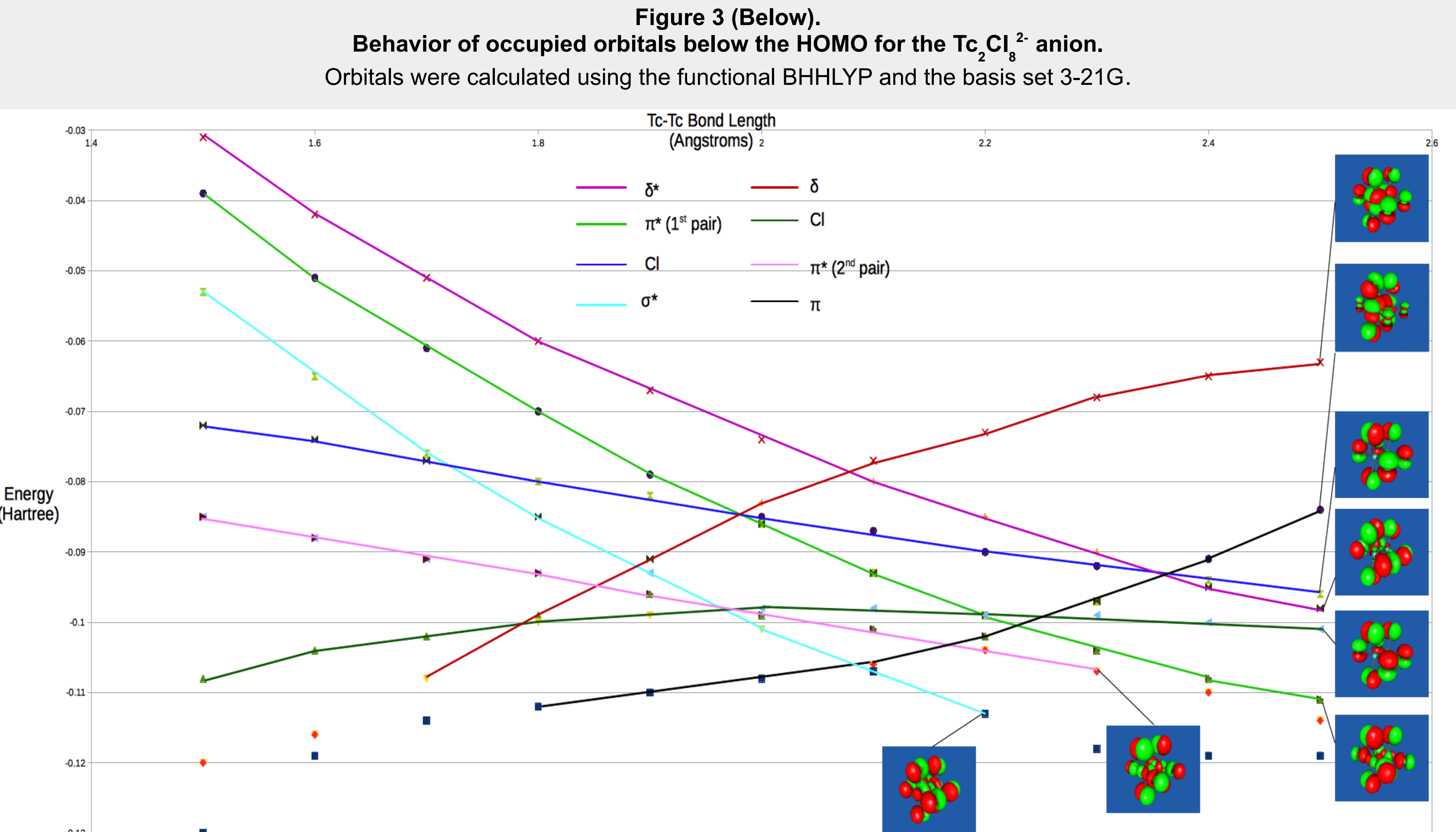


Figure 1. Expected trend between bond order and bond length for the Tc-Tc bond and experimental and theoretical results for the $\text{Tc}_2\text{Cl}_8^{2-/3-}$ anions.

Figure 2 (Above). Differences in Tc-Tc bond length between the $\text{Tc}_2\text{Cl}_8^{2-/3-}$ anions found in reference 2.



	BHHLYP	$\text{Tc}_2\text{Cl}_8^{2-}$	$\text{Tc}_2\text{Cl}_8^{3-}$	Difference
Literature	SDD, aug-cc-pVDZ	2.166	2.120	- .046
Current Project	SRSC, cc-pVDZ	2.1083	2.1191	.0108
	SRSC, aug-cc-pVDZ	2.1064	2.1194	.0130

Figure 6 (Left). Comparison between data from this project and those found in reference 2. The Gaussian SDD is the same ecp as the QCHEM SRSC.

Preliminary Findings

Preliminary results on the ordering of the molecular orbitals (MO) of the $\text{Tc}_2\text{Cl}_8^{2-}$ anion show that the description of the Tc-Tc bond within the $\text{Tc}_2\text{Cl}_8^{2-}$ anion in terms of bond order can be ambiguous. Figure 3 shows the behavior of the highest occupied molecular orbital (HOMO) along with ten more orbitals below the HOMO for the $\text{Tc}_2\text{Cl}_8^{2-}$ anion and Figure 4 shows the resulting MO diagram for the $\text{Tc}_2\text{Cl}_8^{2-}$ anion. This diagram was developed through qualitative examination of the molecular orbitals produced by geometry optimization calculations using the functional BHHLYP and the basis set 3-21G. Figure 5 shows the theoretical MO diagram for the interaction of d orbitals between two metal atoms. The model of bond order predicts that there is only one pair of π^* orbitals near the HOMO, due to interactions with the chlorine atoms in the anion. The bond order of the Tc-Tc bond concerns the MOs involved in the bond between the two Tc atoms. However, many of the MOs that participate in the Tc-Tc bond have some chlorine character. It may be inappropriate to study the behavior of the Tc-Tc bond independently from their interaction with the chlorine atoms.

For the functional that reproduced the experimental trend, our results disagree with the data found in reference 2. Figure 6 shows the comparison between the Tc-Tc bond lengths found from our calculations with those determined in the previous theoretical study. Our data predicts that the Tc-Tc bond length should be longer in the $\text{Tc}_2\text{Cl}_8^{3-}$ anion, while the previous study predicts that it should be longer in the $\text{Tc}_2\text{Cl}_8^{2-}$ anion.

For each of the calculations done using the different combinations of functional and basis set/ecp, graphs of energy plotted against Tc-Tc bond distance were made to determine whether the calculations were carried over a smooth surface. At each variable Tc-Tc bond distance, a geometry optimization calculation was done with a constraint on the Tc-Tc bond distance and no constraints on the rest of the anion. The total energies produced by these calculations were then plotted as a function of Tc-Tc bond length. Figure (7a) shows a calculation that was done across a single surface while Figure (7b) shows a calculation that was done across multiple surfaces. The calculations found in reference 2 were done as geometry optimizations without any constraints. Theoretically, the Tc-Tc bond lengths from those calculations should be the same as the bond lengths found in this project, but it is unsure whether those bond lengths occur at a minimum. The calculations done in reference 2 might or might not have jumped from one curve to another if there are multiple energy-bond length curves for a particular combination of functional and basis set/ecp.

The results on the difference in Tc-Tc bond length between the $\text{Tc}_2\text{Cl}_8^{2-/3-}$ anions for various combinations of functional and basis set/ecp are shown in Figure (8). Results from the calculations done on other anions are also shown. Empty boxes indicate incomplete calculations due to convergence failure or complications with multiple energy-bond length surfaces. The data show that different results are obtained when using different functionals. Moreover, using different basis sets/ecps with the same functional can produce contradictory results. The disagreement between the different calculations suggest that density functionals are inadequate for modeling the behavior of the electrons within the $\text{Tc}_2\text{Cl}_8^{2-/3-}$ anions.

Figure 4. Molecular orbital diagram of the $\text{Tc}_2\text{Cl}_8^{2-}$ anion.

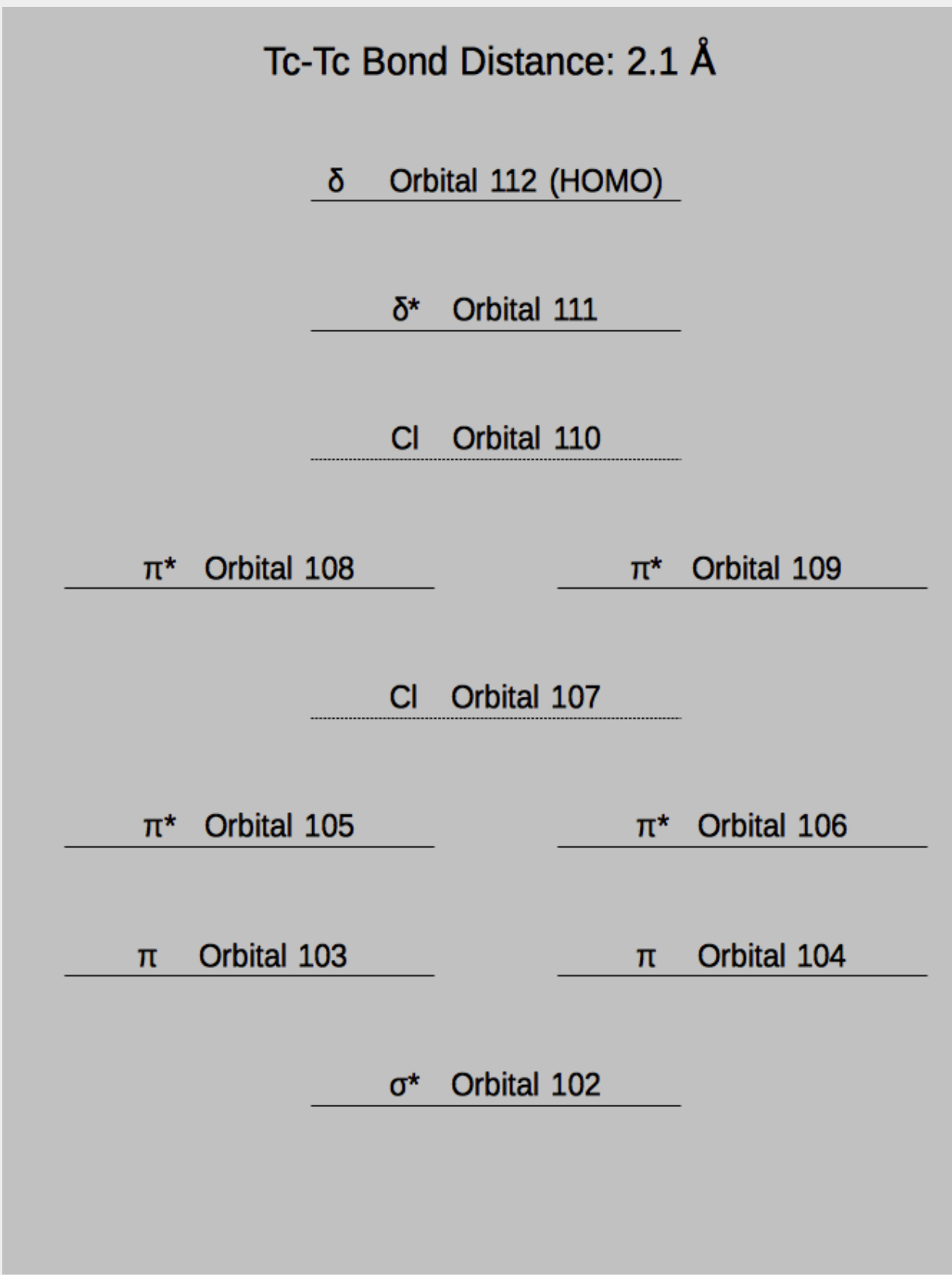


Figure 5.

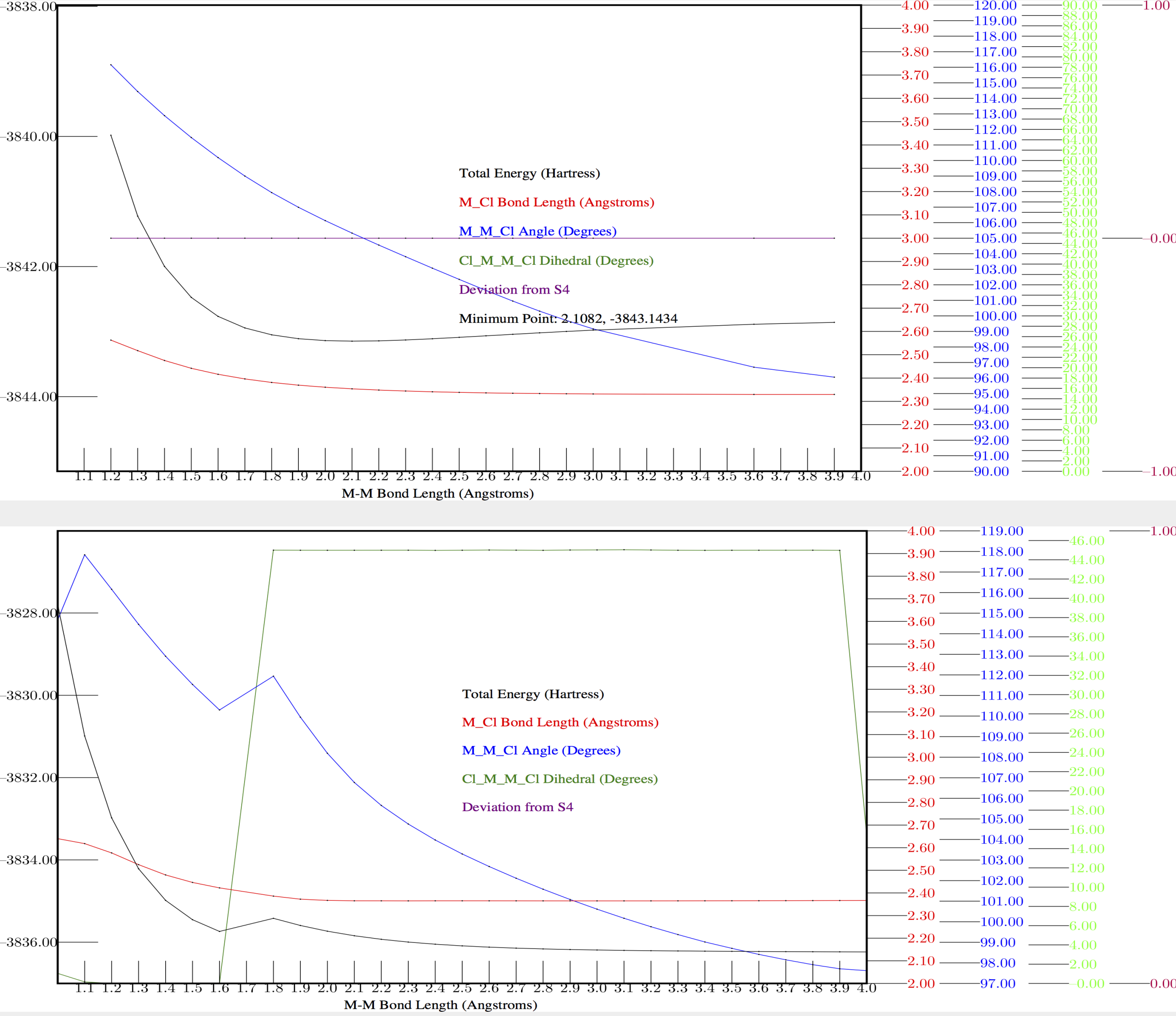
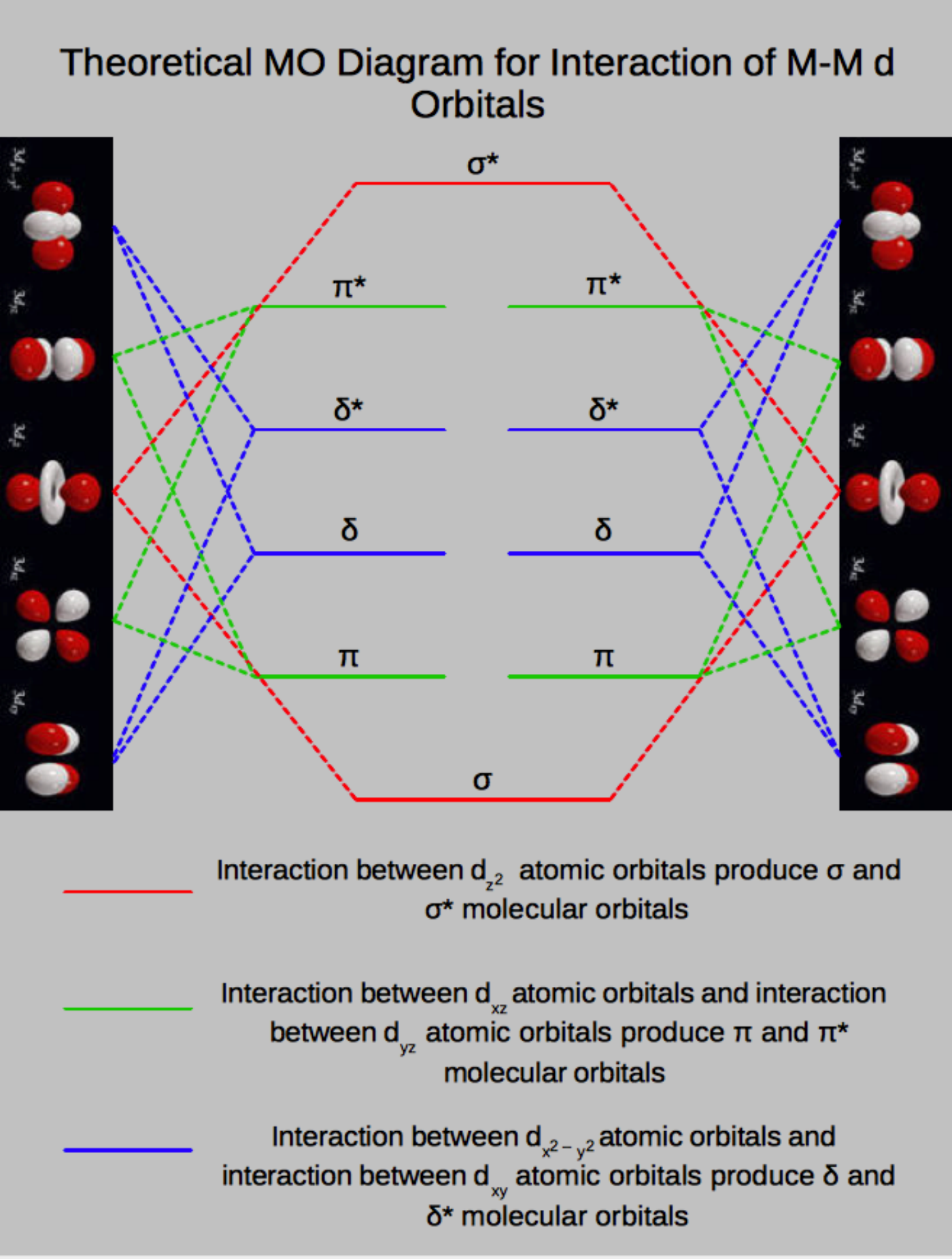


Figure 7a (Top). A sample of a smooth energy versus Tc-Tc bond length curve. Figure 7b (Bottom). Multiple energy-bond length surfaces.

The two figures above show the graphs of energy, M-Cl bond length, M-M-Cl angle, Cl-M-M-Cl, and deviation from S4 as functions of M-M bond length. The top figure shows the graphs for the $\text{Tc}_2\text{Cl}_8^{2-}$ anion as calculated from BHHLYP and SRSC/6-31G. The bottom figure shows the graphs for the $\text{Tc}_2\text{Cl}_8^{2-}$ anion using HF and SRSC/6-31G.

Figure 8 (Below). Differences in M-M bond length between the $\text{Tc}_2\text{Cl}_8^{2-/3-}$, $\text{Mo}_2\text{Cl}_8^{4-/5-}$, and $\text{Ru}_2\text{Cl}_8^{1-/2-}$ anions using various combinations of functional and basis set/ecp. Difference in M-M length found by subtracting bond length in the less reduced anion from the more reduced anion.

		BLYP	B3LYP	BHHLYP
$\text{Tc}_2\text{Cl}_8^{(2-/3-)}$	3-21G	- .0064	- .0025	.0029
	SRSC/6-31G*	- .0017	.0052	.0105
	SRSC/cc-pVTZ	.0023	.0244	
	SRSC/cc-pVDZ		.0037	.0108
$\text{Mo}_2\text{Cl}_8^{(4-/5-)}$	3-21G		.0847	.0542
$\text{Ru}_2\text{Cl}_8^{(1-/2-)}$	3-21G		- .0352	- .1014
	SRSC/6-31G*	- .0392	- .0370	- .0326

Current Research Direction

- From the results of the calculations using different functionals, it is apparent that the nature of the Tc-Tc bond within the $\text{Tc}_2\text{Cl}_8^{2-/3-}$ anions cannot be adequately explained by examining solely the behavior of the molecular orbitals involved in the Tc-Tc bond.
- The results of the CCSD calculations will be analyzed using singular value decomposition (SVD) in order to extract the most import features of the electron correlations within the $\text{Tc}_2\text{Cl}_8^{2-/3-}$ anions. From the information gained from SVD, a model that is more robust than the simple model of bond order will be made for the behavior of these anions.

References

1. Poineau F., Forster P. M., Todorova T. K., Gagliardi L., Sattleberger A. P., Czerwinski K. R. "Multi-configurational quantum chemical studies of the $\text{Tc}_2\text{Cl}_8^{2-}$ (X = Cl, Br; n = 2, 3) anions. Crystallographic structure of the octabromoditechnetate(3)." *Dalton Trans.*, **41**, 2869, 2012.
2. Pastor M., Zhao, Q. "A DFT Investigation on the Electronic Properties of Octahaloditechnetate Anions: Correlation between Charge and Bond Strength." *Inorg. Chim. Acta*, **424**, 308, 2015.

Acknowledgements

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