

Investigations into the Nature of Dimetallic Bonds within Octachlororditechnetate Anions ($\text{Tc}_2\text{Cl}_8^{2-}$) using Computational Methods

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Overview

Molecules involve groups of atoms held together through the interaction between the atoms' electrons. The behavior of these electrons can be represented by quantum mechanical wave functions, or mathematical models, 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.

A conventional view of bonding involves a concept called "bond order." Calculation of bond order involves comparing the number of electrons found within bonding orbitals with those found within antibonding orbitals. In the conventional view of bonding, molecular orbitals can be classified as either bonding or antibonding based on qualitative analysis of pictorial representations of the orbitals. When an orbital contains an increase in electron density between two atoms (Figure 3a), that orbital contributes to the bonding between the atoms. If an orbital involves a decrease in electron density between two atoms (Figure 3b), that orbital contributes to the antibonding between the atoms.

A general "rule" relates bond order with the length of a bond. An increase in bond order usually accompanies a decrease in bond length. However, a published article¹ has found a case that deviates from this prediction. In the case of the octachloroditechnetate ($\text{Tc}_2\text{Cl}_8^{2-}$) anions (Figure 1), as bond order increases, the bond length also increases, contrary to expectations. The authors of the paper calculated the bond order of these anions under the assumption that the conventional view of bonding adequately accounts for the behavior of the octachloroditechnetate anions. It should be noted that the concept of bond order represents a very basic approximation of the nature of the bonds between atoms. This view assumes that each 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.

The initial direction of this project was to develop an energy level diagram for the molecular orbitals of the $\text{Tc}_2\text{Cl}_8^{2-}$ anion that would provide an explanation for the observed relationship between bond order and bond length within the $\text{Tc}_2\text{Cl}_8^{2-}$ anion. From the energy level diagram developed, it would then be determined how an increase in bond order would lead to an increase in bond length. Calculations of orbital geometries were carried out using QCHEM and pictorial representations of the orbitals were made on IQmol (Figure 3). Orbitals around the highest occupied molecular orbital (HOMO) were classified as sigma (σ), pi (π), or delta (δ) bonding orbitals or as σ^* , π^* , or δ^* antibonding orbitals. Some orbitals were classified as being localized around the chlorine atoms or as diffuse (Figure 2). From the preliminary molecular orbital diagrams that were developed using the models HF, CAM-B3LYP, and LDA, no obvious pattern could be determined (Figure 4) to make a general energy level diagram for the $\text{Tc}_2\text{Cl}_8^{2-}$ anion.

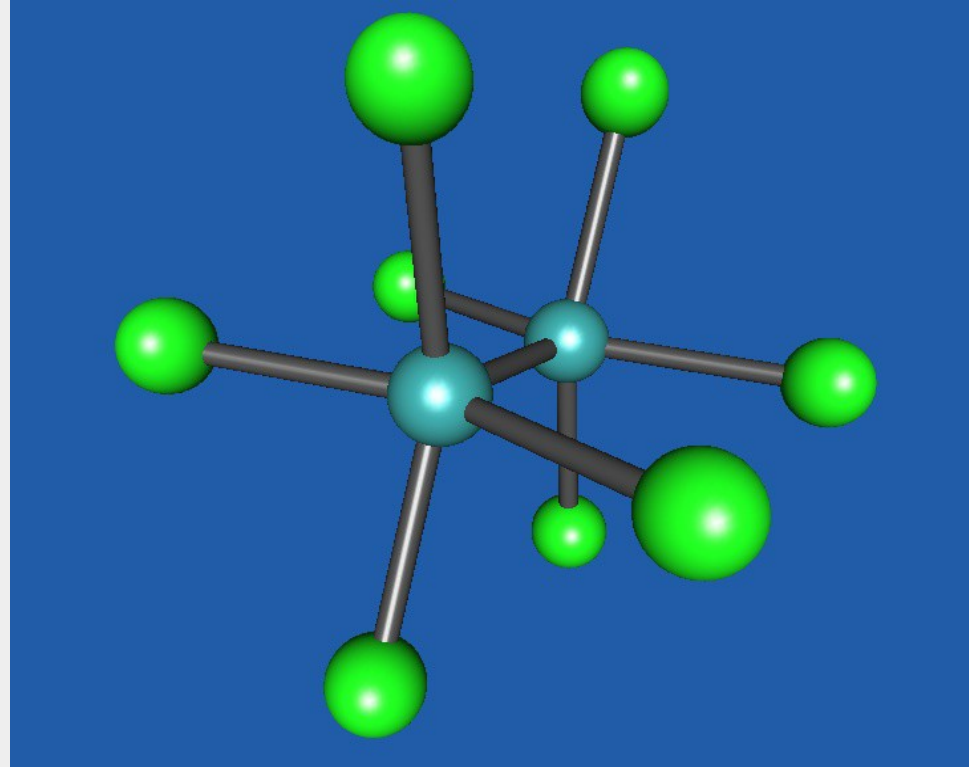


Figure 1 (Left). The Octachloroditechnetate ($\text{Tc}_2\text{Cl}_8^{2-}$) Anion.

Blue: Technetium atom.
Green: Chlorine atom.

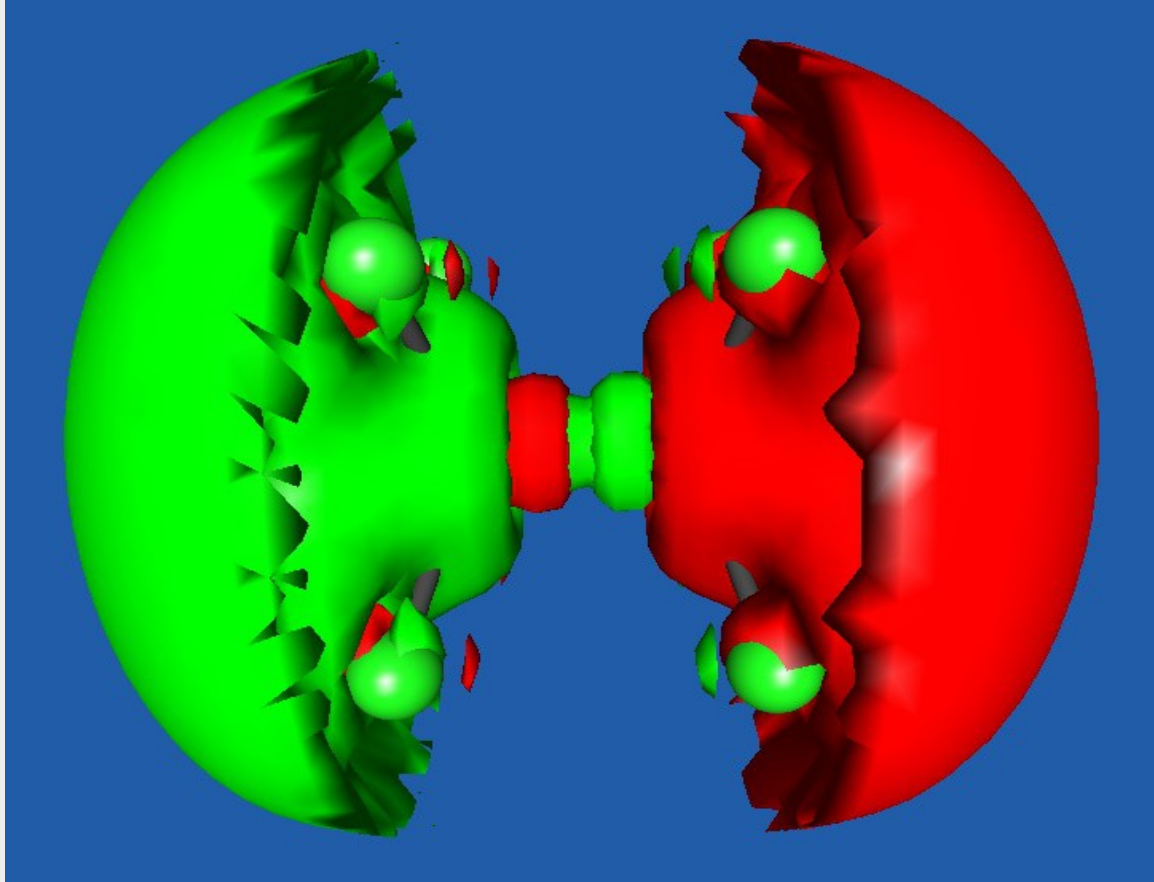
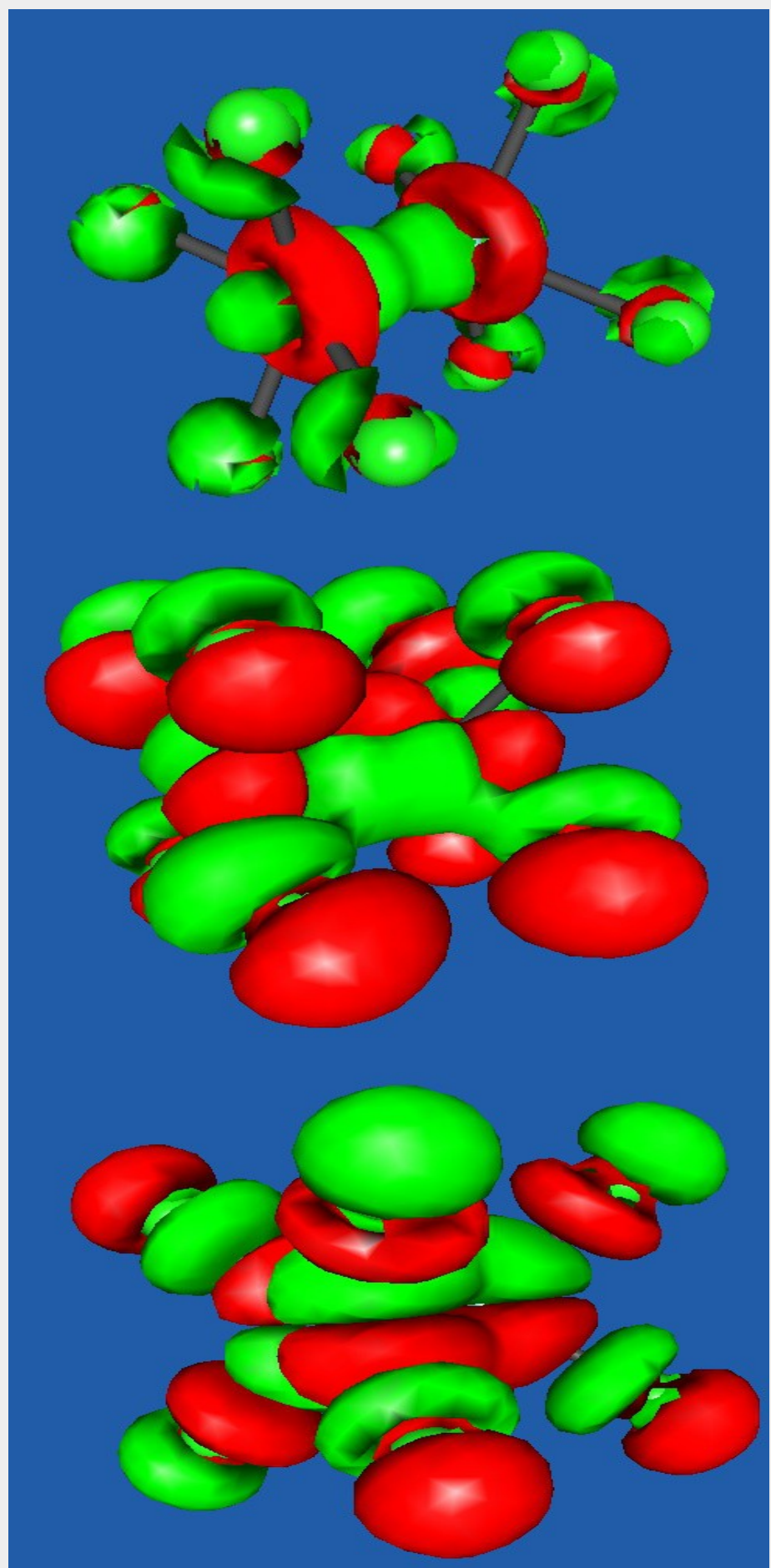


Figure 2 (Right). A sample diffuse orbital.

Figure 3 (Bottom). Sample $\text{Tc}_2\text{Cl}_8^{2-}$ Orbitals.

a) Bonding Molecular Orbitals.
Top to bottom: σ , π , δ



b) Antibonding Molecular Orbital.
Top to bottom: σ^* , π^* , δ^*

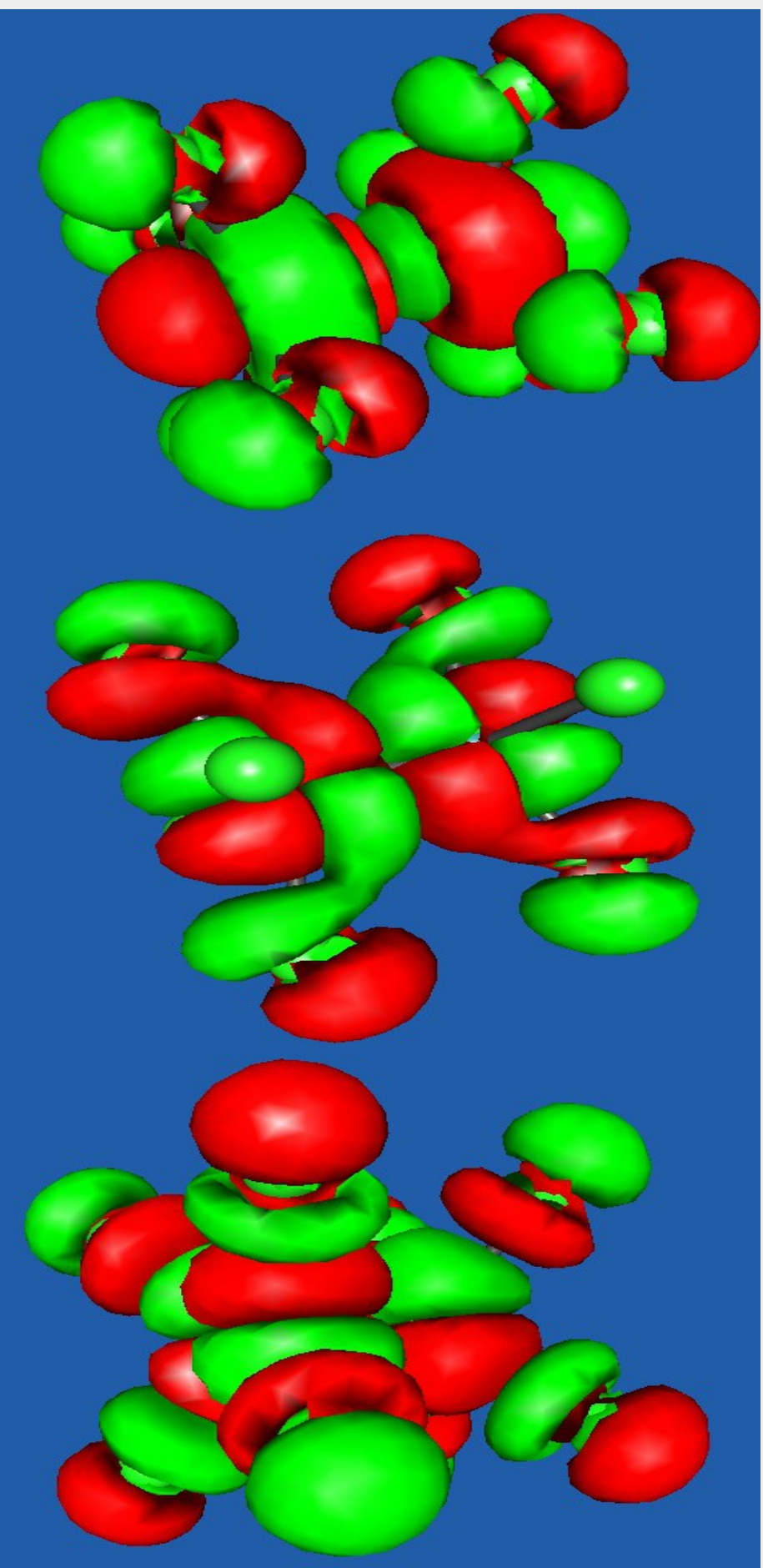


Figure 4 (Bottom). Orbitals Near the Highest Occupied Molecular Orbital (HOMO = 112) in $\text{Tc}_2\text{Cl}_8^{2-}$ Calculated Using Various Models.

π^* (-4.95)
Orbital Type (Energy in eV)

σ : Sigma Bonding Orbital
 π : Pi Bonding Orbital
 δ : Delta Bonding Orbital
Cl : Chlorine-localized Orbital
D : Diffuse Orbital

σ^* : Sigma Antibonding Orbital
 π^* : Pi Antibonding Orbital
 δ^* : Delta Antibonding Orbital

| | | HF | CAM-B3LYP | LDA |
|-------------------|------|--------------------|--------------------|--------------------|
| Molecular Orbital | | | | |
| 100 | | π^* (-4.95) | π (-3.02) | δ^* (-.707) |
| 101 | | π^* (-4.95) | π (-3.02) | π (-.571) |
| 102 | | σ (-4.93) | σ (-2.88) | π (-.571) |
| 103 | | σ^* (-4.82) | π^* (-2.78) | π^* (-.299) |
| 104 | | Cl (-4.57) | π^* (-2.78) | π^* (-.299) |
| 105 | | δ^* (-4.54) | π^* (-2.48) | π^* (-.109) |
| 106 | | Cl (-4.38) | π^* (-2.48) | π^* (-.109) |
| 107 | | δ (-4.30) | Cl (-2.34) | π (.109) |
| 108 | | π^* (-3.78) | Cl (-1.90) | π (.109) |
| 109 | | π^* (-3.78) | π (-1.71) | Cl (.299) |
| 110 | | δ^* (-3.59) | π (-1.71) | Cl (.327) |
| 111 | | π (-3.13) | δ (-.980) | Cl (.490) |
| 112 | HOMO | π (-3.13) | δ^* (-.136) | δ (.036) |
| 113 | | Cl (.109) | Cl (.354) | δ^* (.980) |
| 114 | | D (7.40) | π^* (6.18) | π^* (3.16) |
| 115 | | σ^* (7.73) | π^* (6.18) | π^* (3.16) |
| 116 | | π^* (7.76) | σ^* (6.18) | δ (3.46) |

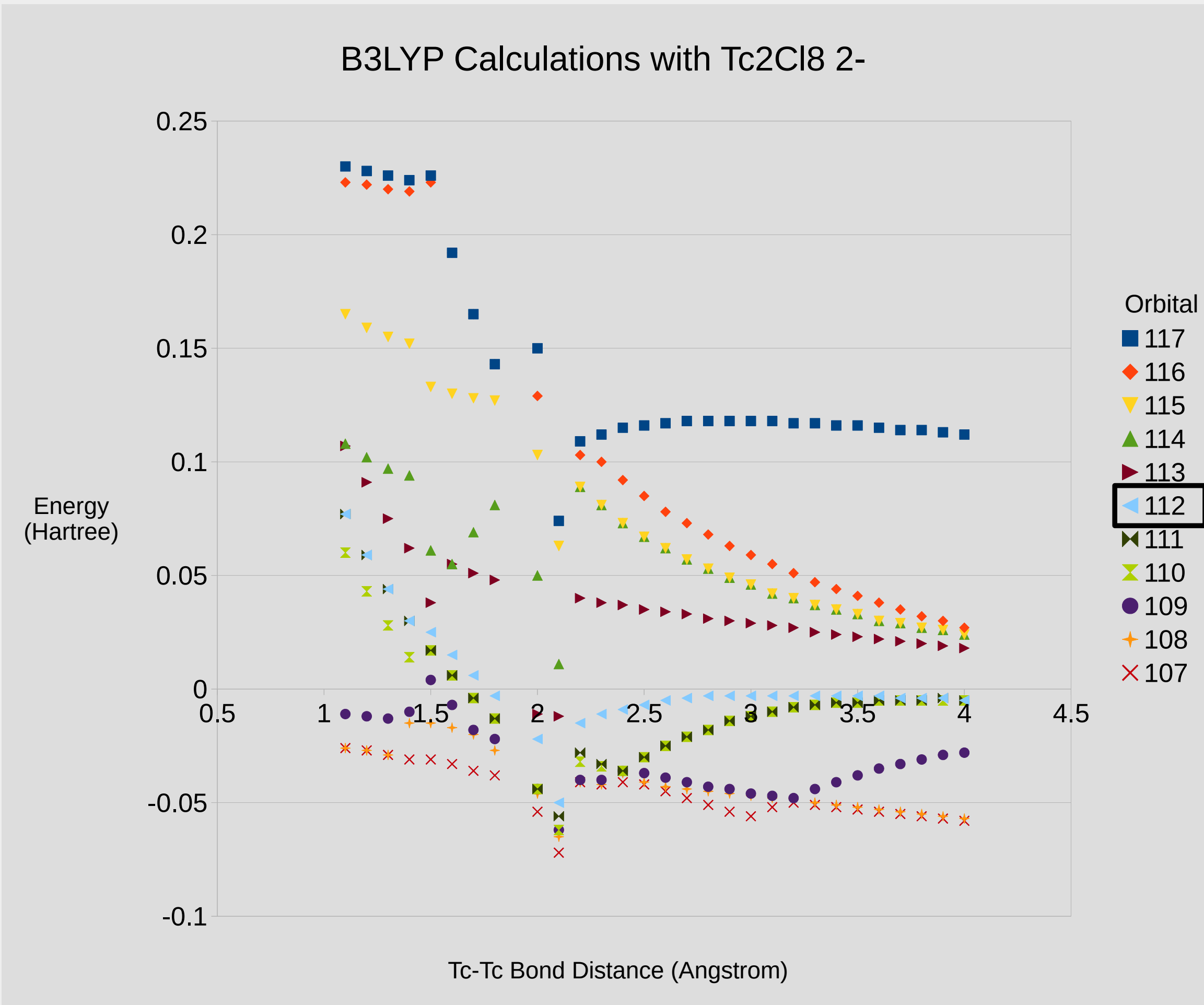
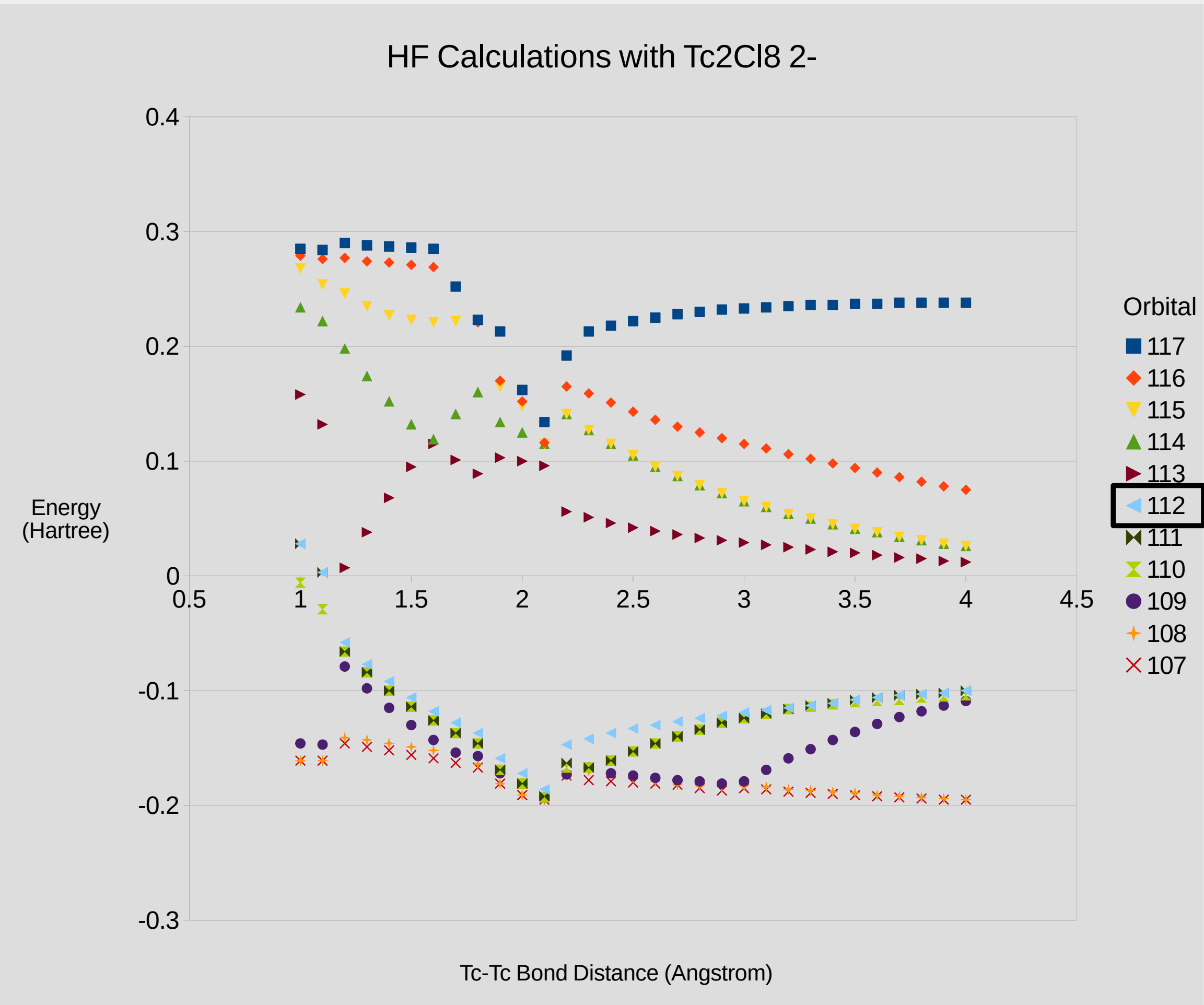


Figure 5. $\text{Tc}_2\text{Cl}_8^{2-}$ Orbital Energies as a Function of Bond Distance. Tc-Tc: Technetium-Technetium.

Preliminary Findings

From the results of the calculated molecular orbital energies and geometries, it was decided that a different approach was needed in order to describe the nature of the technetium-technetium (Tc-Tc) bond. The concept of bond order is valuable in that it provides a simplified view of how atoms interact with each other within molecules. However, while bond order works well for simple diatomic molecules such as molecular oxygen (O_2) and molecular nitrogen (N_2), bond order does not work well with more complex systems such as the $\text{Tc}_2\text{Cl}_8^{2-}$ anion.

Another method of describing the behavior of the Tc-Tc bond within the $\text{Tc}_2\text{Cl}_8^{2-}$ anion involves describing the molecular orbitals within the anion in terms of changes in energy in relation to changes in the Tc-Tc bond length (Figure 6). An orbital in which the energy decreases as bond length decreases is defined as a bonding orbital and contributes to the bonding between two atoms. An orbital in which the energy increases as bond length decreases is defined as an antibonding orbital and contributes to the antibonding between two atoms. An orbital in which the energy does not change as bond length changes is defined as a nonbonding orbital and does not contribute to either the bonding or the antibonding between two atoms.

The energies of different orbitals can be graphed as a function of bond distance in order to determine whether each orbital contributes to the bonding, antibonding, or nonbonding between the technetium atoms within the $\text{Tc}_2\text{Cl}_8^{2-}$ anion.

Preliminary graphs of orbital energy as a function of Tc-Tc bond distance (Figure 5) show that the orbitals around the HOMO behave strangely at around a Tc-Tc bond distance of 2 Angstrom. The Tc-Tc bond distance of 2 Angstrom is the observed Tc-Tc bond distance within the $\text{Tc}_2\text{Cl}_8^{2-}$ anion reported by the previously mentioned published paper. There might be some property related to this particular bond distance within the $\text{Tc}_2\text{Cl}_8^{2-}$ anion that lead to the strange relationship between bond order and bond length found by the authors of the paper. This project hopes to investigate further into the nature of the Tc-Tc bond through examination of the $\text{Tc}_2\text{Cl}_8^{2-}$ anion's molecular orbitals in terms of changes in energy in relation to changes in bond distance.

Current Research Direction

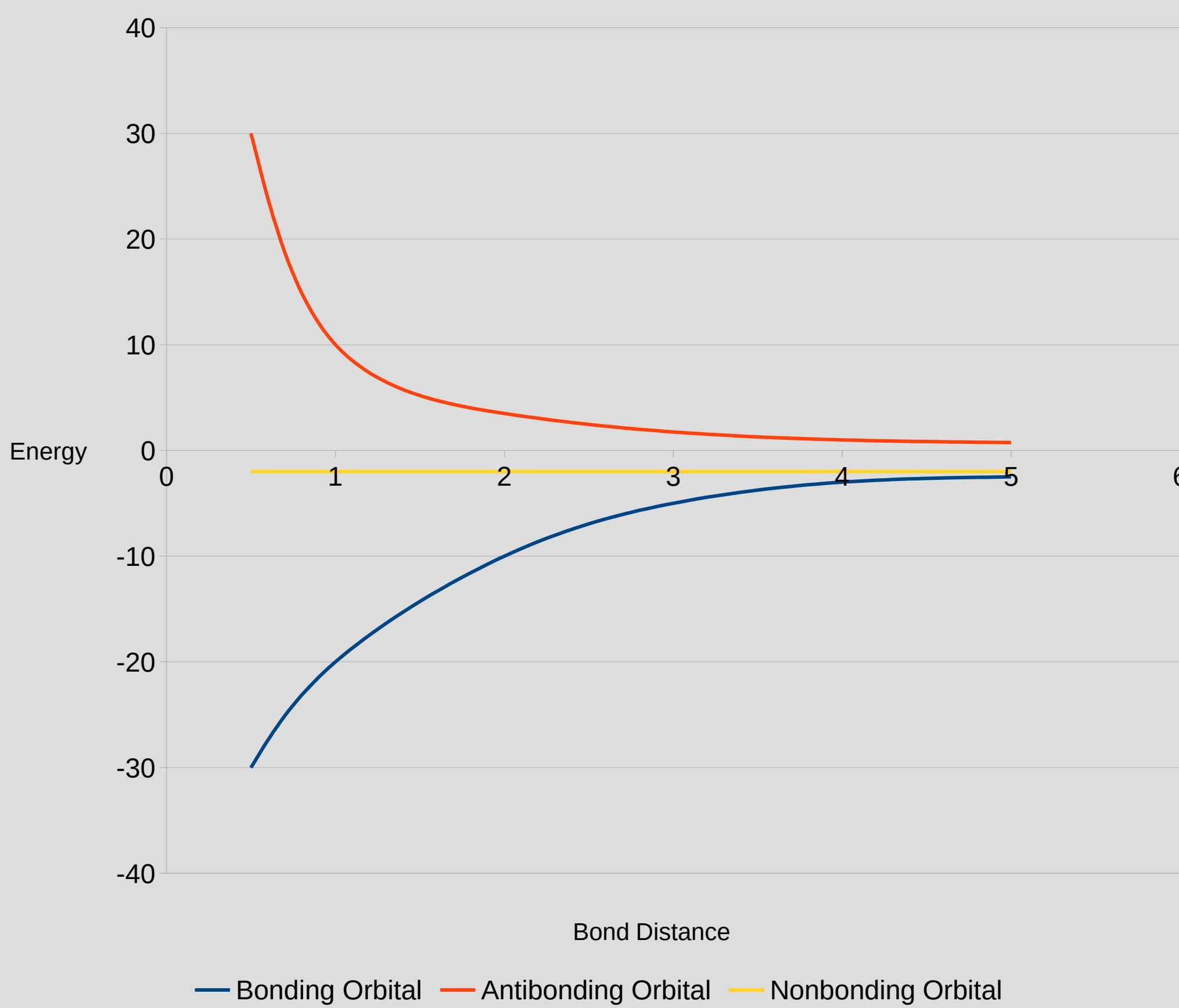
- Molecular orbital energies of the $\text{Tc}_2\text{Cl}_8^{2-}$ anion will be calculated using the models BLYP, BH&HLYP, PBE, and SVWN
- Orbital energies will be graphed as a function of Tc-Tc bond distance
- The bonding, antibonding, or nonbonding character of each orbital will be noted and compared between each of the different models
- A hypothesis concerning what might be influencing the strange behavior of Tc-Tc bond will be developed using the aspects that are common amongst the different models

Figure 6.

Representative bonding, antibonding, and nonbonding orbitals.

Blue: Bonding orbital. Energy decreases as bond distance decreases.
Red: Antibonding Orbital. Energy increases as bond distance decreases.
Yellow: Nonbonding orbital. Energy does not change with change in bond distance.

Graphs of Hypothetical Orbital Energy as Function of Bond Distance



Acknowledgements

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Michael Pastor

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 $\text{Tc}_2\text{Cl}_8^{2-}$ ($X = \text{Cl}, \text{Br}; n = 2, 3$) 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."