A Density Functional Theory Calculation Study of Hybrid Perovskite Materials

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Introduction

- With increasing global population, alternative energy sources are of interest to sustain the growing energy demand.
- Solar energy, along with wind, biomass, and tidal sources are an answer to our energy requirements, as they are freely available and generally less polluting than conventional fossil fuels.[1]
- Solar technology
  - Common technologies in the sector include crystalline and amorphous silicon, and cadmium telluride (CdTe).[2]
  - Cadmium is highly toxic and telluride has low earth abundance.[1]
- Hybrid perovskites are a revolutionizing photovoltaic material.
  - They are in the form ABX_3, where A = Methylammonium (MA^+), B = Sn^{2+}or Pb^{2+}, and X = Cl^-, Br^-, or I^-.[3]
- Methylammonium lead iodide ($MAPbI_3$) perovskites have dominated the research field over the past decade.
  - Reaching a high photoconversion efficiency of approximately 22%.[5]
  - Unfortunately, Pb is a toxic element, therefore tin (Sn) could be a non-toxic replacement.[5]
- Solid-state nuclear magnetic resonance (NMR) spectroscopy is a technique used to provide insight into atomic-level structure and dynamics of solids.[6]
- Density functional theory (DFT) is a type of quantum chemical calculation that can be used to calculate NMR parameters.

Purpose/Goal

- Assess calculated chemical shielding values (σ) for model compounds $[SnX_6]^{-4}$ (Figure 3) to those obtained experimentally for $MASnX_3$ compounds (X = Br^-, I^-, Cl^-) (Figure 1)
- Evaluating the effect of chosen basis set with and without relativistic effects (ZORA) on calculated shielding tensors will be discussed.

Method/Experiment

Quantum Chemical Calculations:

- DFT calculations were performed via ADF modelling suite.[7]
- Basis sets: TZ2P, and QZ4P (relativistic (ZORA) and non-relativistic (without ZORA))
- Molecular-based structure simulated via crystallographic data

Crystal Structures of $MASnX_3$

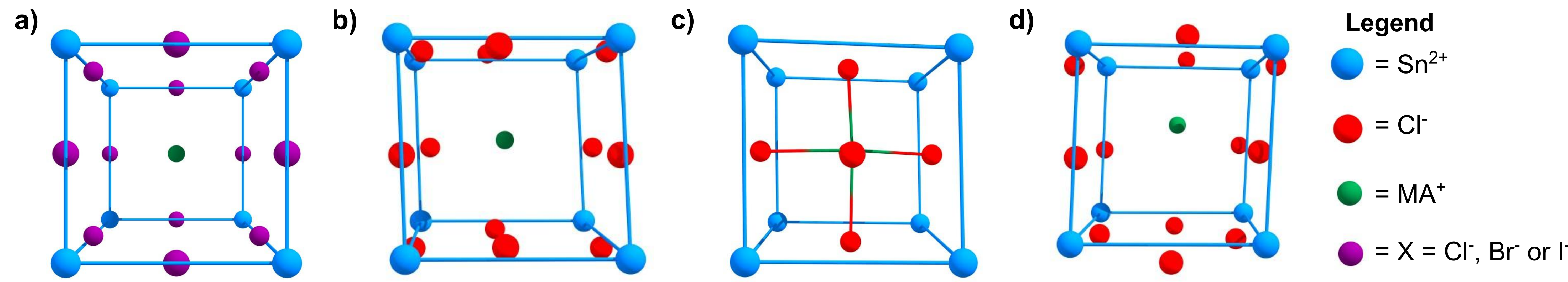

Figure 1: Crystal structure of $MASnX_3$ complexes:
a) cubic
b) rhombohedral
c) monoclinic
d) triclinic

Experimental Results

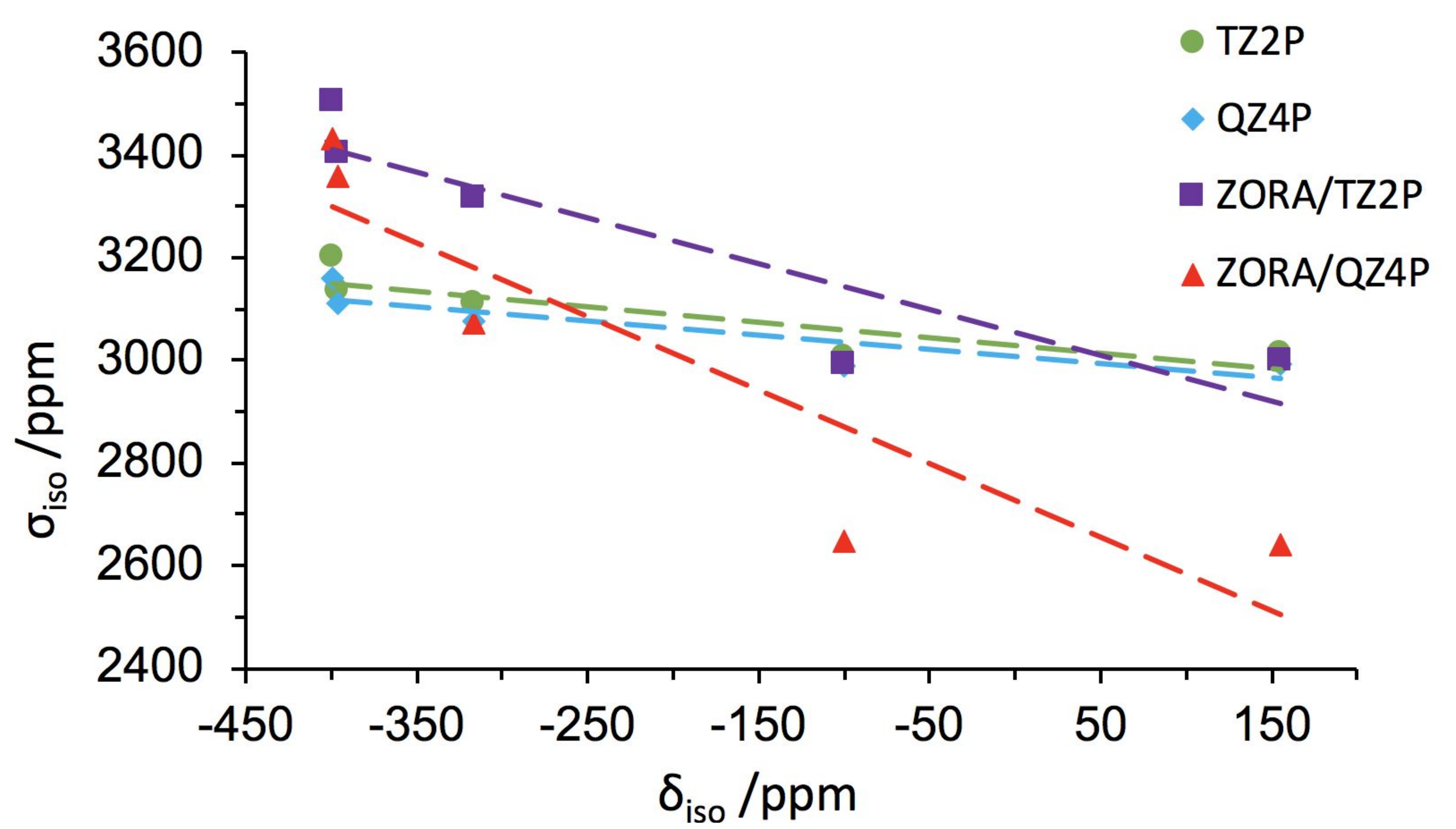

Figure 2: Plot of experimental ^{119}Sn isotropic chemical shifts (δ_{iso}/ppm) with the corresponding DFT calculated isotropic shieldings (σ_{iso}/ppm). Data from the rhombohedral structure of $[SnCl_6]^{-4}$ was omitted due to its anomalous nature (further studies underway).

Table 1: R^2 values for trendlines in Figure 2

Basis Set	R^2 Value
TZ2P	0.7605
QZ4P	0.7676
ZORA/TZ2P	0.8212
ZORA/QZ4P	0.8223

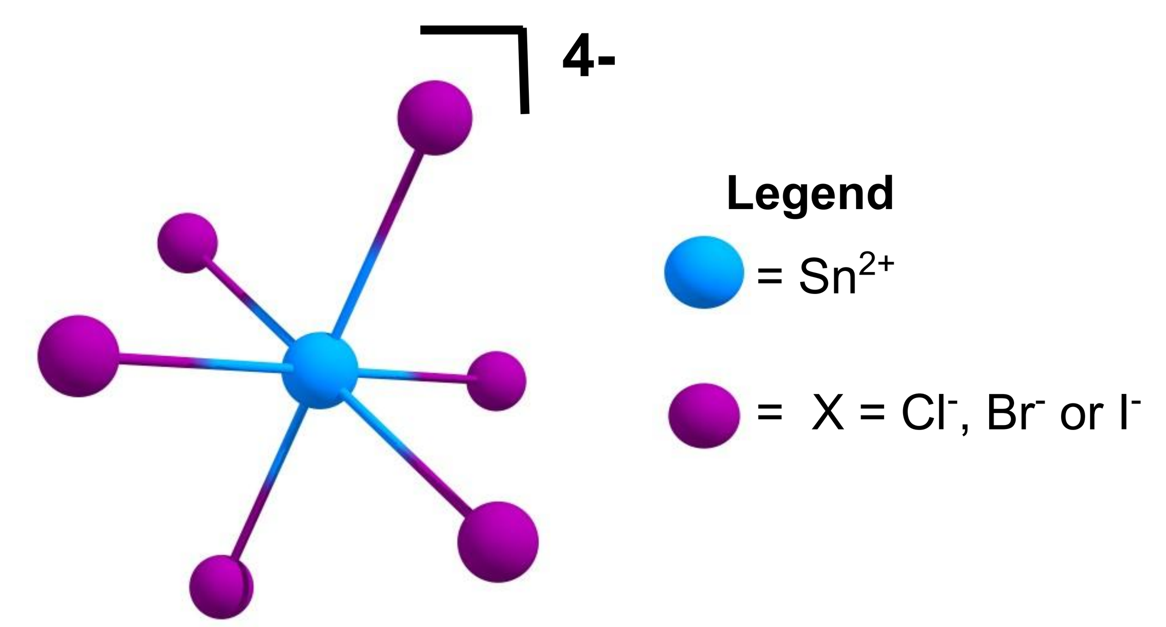

Figure 3: Anionic computational model $[SnX_6]^{4-}$

Conclusion/Future Work

- Shielding values obtained via ZORA/QZ4P basis set most accurately reproduce the observed experimental data.
- ZORA/TZ2P and ZORA/QZ4P had similar R^2 values.
  - Either are valid basis sets to use depending on the limit placed on computational time and space.
    - CPU time for ZORA/TZ2P < ZORA/QZ4P (factor of ~ 2).
- Future works:
  - Comparison of anionic model complex vs. crystal structure.

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