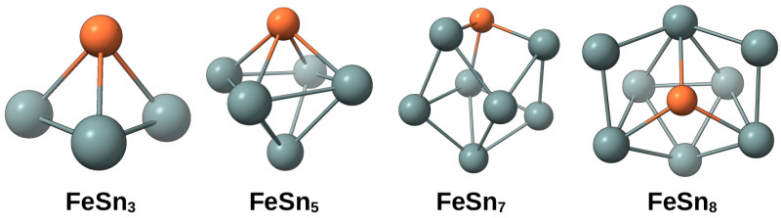
Hessisches Kompetenzzentrum
für Hochleistungsrechnen

Properties of Iron-Tin Clusters



Project Manager
Carlos M. Jimenez-Muñoz

Principal Investigator
Prof. Dr. Vera Krewald

Project Term
2022 - 2023

Clusters
Lichtenberg II Cluster Darmstadt

Software
ORCA

Additional Software
MPI, SHARC

Institute
Quantum Chemistry

University
Technische Universität Darmstadt

Introduction

For transition metal doped clusters, the transition metal and the host element play a fundamental role in the physical and chemical properties of the material. These materials' composition- and size-dependent nature makes them promising systems for developing nano-structured magnetic materials among other advanced materials. Our motivation was to explore the structures and electronic properties of iron-tin clusters $FeSn_x$, x = 3 − 22, in relevant spin states and to define theoretical approaches for precisely predicting ionization energies.

Methods

Trial structures for different cluster sizes were obtained from the literature and a genetic algorithm (GIGA) was used.[1] The ground state structures, oxidation state, and spin states of these clusters were predicted with high-level computational methods (DLPNO- CCSD(T)).
As the computational cost of high-level methods grows exponentially with the size of the system, we designed less expensive methods based on density functional theory (DFT) at a similar level of accuracy as the higher-level methods. Experimental data served as a benchmark for the predicted ionization potentials and magnetic properties at different levels of theory.
The Wigner sampling method allowed the exploration of vibrational effects near the energy minimum of each structure. This approach triggers or quenches molecular effects beyond the energetic minimum on the potential energy surface (PES) and describes molecular properties more realistically.

Results

The structures generated by GIGA (around 1500 structures per cluster size) were clas- sified according to the bond lengths aiming to find isomeric structures and avoid any double counting. The group of isomers was sorted against the lowest energy structure and with 1eV as the upper limit.
Molecular properties were predicted at the DFT level using the ORCA software package. For each cluster size, four possible multiplicities were chosen: singlet, triplet, quintet, and septet. The trend of spin-state energetics for cluster sizes from 3 to 12

tin atoms vs the relative energy is shown in Figure 2. The energy for multiplicities 1 and 7 are too high, but multiplicities 3 and 5 are very close in almost all cases (less than 5 kcal/mol).
The high-precision electric beam deflection experiments performed by the group of Prof. R. Schäfer yielded a simulated beam profile that reveals critical details about the measured gas-phase clusters, including properties such as the ionization potential (IP), geometry (symmetry), dipole moment, and the g-factor.
The IP for the ground state of DFT-generated structures was predicted at the DLPNO- CCSD(T_1) level (3 to 8 tin atoms) and used to benchmark suitable DFT protocols. In Figure 3, a correlation curve between DLPNO-CCSD(T_1) (3 to 8 tin atoms) and the best-matching DFT protocol is shown for the two multiplicities predicted before. Other DFT methods tested are shown in the tables on the right side of the figure. After the comparison, there is a small energy inconsistency (less than 1eV) between the predicted IP and the experimentally measured value. This can be explained by a wrong geometry or symmetry prediction, or an incorrect electronic structure.
The profiles simulated using our predicted ground-state structures showed a quenched profile that does not fit with the experiment, however, the DFT calculations predicted low-lying vibrational states (less than $30 cm^{-1}$).
The experimental electric deflection data strongly depend on the permanent electric dipole moment of the cluster. We implemented the Wigner quantum harmonic oscillator distribution, available as part of the SHARC package, and sampled initial conditions for the ground state structure of $FeSn_8$, generating an ensemble of structures that includes the low-lying vibrational effects. In Figure 4, the Wigner ensemble and the distribution of dipole moments for the ground state structure of the system $FeSn_8$ are shown.

Discussion

From the experimental side, the effect of low-lying vibrational states is being implemented with molecular dynamics simulations. This insight might explain the experimental results, as it introduces structural flexibility due to the low-lying modes and temperature dependence on the electronic properties of the clusters.
For future work, the electronic structure of the ground state geometry for each cluster size must be studied in detail. From the theoretical side, implementing Complete Active Space Self-Consistent Field (CASSCF) calculations is the next step.

Figures

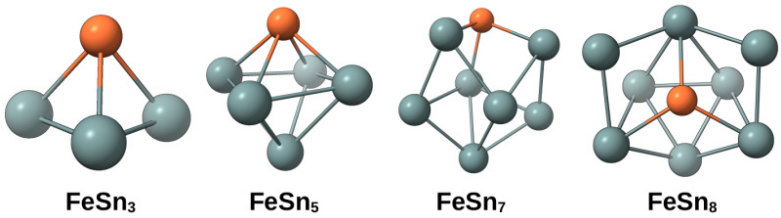


Figure 1: Potential cluster geometries for the smaller cluster sizes

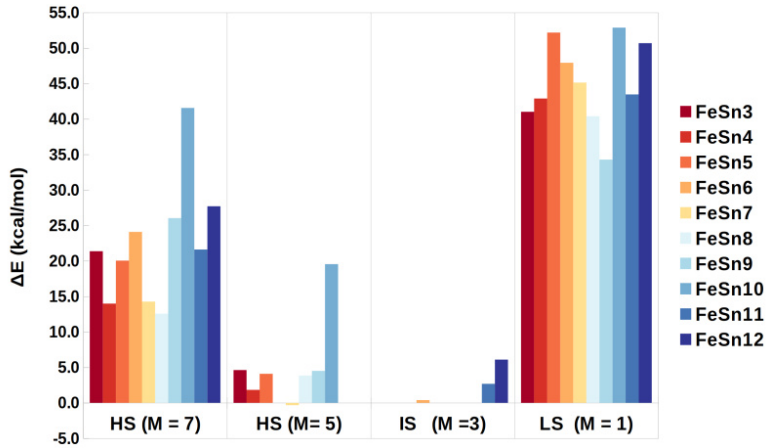
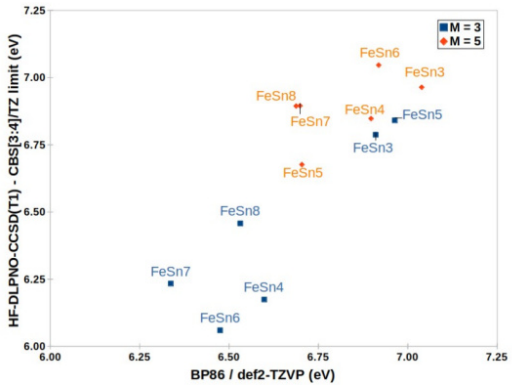


Figure 2: Spin-energetics for $FeSn_x$ cluster with x = 3 - 12



PBE0 / def2-TZVP	M =5	M = 3
FeSn3	6.63	6.69
FeSn4	6.82	6.52
FeSn5	6.86	6.91
FeSn6	6.78	6.23
FeSn7	6.66	6.29
FeSn8	6.70	6.35

B3LYP / def2-TZVP	M =5	M = 3
FeSn3	7.16	6.62
FeSn4	6.74	6.34
FeSn5	6.68	6.77
FeSn6	6.72	6.16
FeSn7	6.52	5.67
FeSn8	6.69	6.20

TPSSh / def2-TZVP	M =5	M = 3
FeSn3	6.72	6.76
FeSn4	6.85	6.51
FeSn5	6.96	6.88
FeSn6	6.83	6.18
FeSn7	6.66	6.47
FeSn8	6.62	6.43

Figure 3: Ionization potential prediction of $FeSn_x$ clusters (x = 3 - 8)

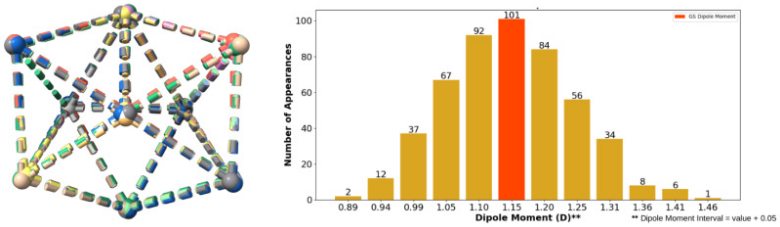


Figure 4: Wigner sampling dipole moment distribution for $FeSn_8$

Publications

Jimenez-Muñoz, C. M. Summer School ”Modern Wavefunction Based Methods in Electronic Structure Theory (MWM23)”, Prediction of Ionization Energies for Iron-Tin Clusters, Pisa - Italy, August 27th - September 2, 2023

Jimenez-Muñoz, C. M. Summer School ”Spectroscopy and Electronic Structure of Transition Metal Complexes”, Prediction of Ionization Energies for Iron-Tin Clusters, Gelsenkirchen - Germany, September 24 - 29, 2023

Jimenez-Muñoz, C. M. Quo Vadis – overarching goals?! - CRC 1487 Annual General Assembly, Probing and understanding physicochemical properties of Iron-Tin Clusters, Johannes- berg - Germany, October 4 - 6, 2023

Reference

Jäger, M; Schäfer, R; Johnston, R. L. GIGA: A versatile genetic algorithm for free and supported clusters and nanoparticles in the presence of ligands. Nanoscale, 11(18):9042–9052, 2019. https://doi.org/10.1039/C9NR02031D

Last Update: 2024-10-10 17:19