Investigation of Spin Isomers in Sn_NFe with N = 8-16

Project Manager
Filip Rivic

Researchers
Andreas Lehr

Principal Investigator
Prof. Dr. Rolf Schäfer

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Clusters
Lichtenberg II Cluster Darmstadt

Software
GAUSSIAN, ORCA

Institute
Eduard-Zintl-Institut

University
Technische Universität Darmstadt

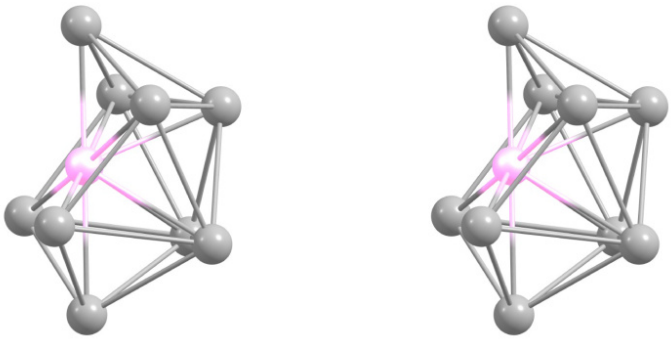


Figure 1: Calculated geometric structures of the spin isomers (Iso) of Sn_9Fe with the corresponding label containing the multiplicity, the relative energy, the symmetry and electric dipole moment in Debye. The tin atoms are displayed as gray spheres and the iron atom in pink. Both isomers show a very similar geometric structure. However, the electric dipole moment of the quintet isomer is nearly three times larger than the one of the triplet (GM).

Introduction

In the framework of the Collaborative Research Center (CRC 1487), iron is studied as a substitute for rare-earth metals in environmental-friendly technologies, since the rare-earth metals are toxic or obtained by disputable methods. For this, it is required to investigate iron in different environment in order to reveal its characteristics. Small doped tin clusters are very suitable systems because their behavior are often tunable by the number of tin atoms. We have already investigated neutral Sn_NFe clusters with $N = 8\text{-}16$ with a spin multiplicity of $S = 2$ (quintet) in order to compare the quantum chemical results with experimental data. However, multireference calculation of the Sn_8Fe from another group at the TU Darmstadt suggest, that this cluster species possesses a spin multiplicity of $S = 1$ (triplet). Therefore, we wanted to investigate the possibility of different spin multiplicities for all possible structural candidates generated by a genetic algorithm [2]. Based on that, a deeper understanding of the magnetic and electric interplay between the diamagnetic host cage and the paramagnetic dopant is obtained.

Methods

From a pool of structural candidates generated by a genetic algorithm developed in our group [2] geometrical isomers in the range of 1 eV relative to the energy of the energetically lowest-lying geometry are optimized on the PBE0/def2-TZVPP level of theory. The existence of local minima has been verified by

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frequency analysis. These calculations were carried out with the quantum-chemical program Gaussian16. For some cluster sizes the geometry optimization were also carried out with ORCA 5.0.4 to compare the results and rule out influences from the codes used to calculate the final geometric structures and energies.

Results

At first, the structural candidates of $Sn_{11}Fe$ cluster were identified with multiplicities of *S = 1* (triplet), 3 (septet) and 4 (nonet) (*S = 2* was already identified in the previous project [2]) and their energies were compared to the value of the global minimum (GM). Here, we could observe that the energy of the calculated geometries depend strongly on the spin multiplicity, resulting in energies differences up to 3 eV relative to the GM for the highest multiplicity, making these spin isomers the most improbable structures to be present in the experiment. The septet isomers also showed very high energies of up to 2 eV with respect to the GM. None of the calculated candidates with nonet and septet multiplicity was found in the energy range of 0.2 eV which is considered to be relevant in comparison to our experiment. However, the calculations of the triplet isomers showed similar and sometimes even lower energies compared to the quintet, confirming the results of the multireference calculations on the Sn_8Fe cluster. Based on this observation, we systematically studied the triplet isomers for the Sn_NFe clusters with *N = 8-16*.

Discussion

By investigating the triplet isomers of the clusters mentioned above, at least one triplet isomer was found in the energy range of 0.2 eV compared to the GM for all considered cluster sizes except for the $Sn_{12}Fe$. In case of the clusters with *N = 8-10* and 13, the triplet isomers are the new GM. For some cluster sizes, the quintet and triplet isomers posses very similar geometric structures. However, the dielectric properties are considerably different. Measuring the electric dipole moment allows then not only to discriminate the geometric structure but also the spin multiplicity of the cluster.

Reference

[1] Rivic, F.; Lehr, A.; Schäfer, R.: "Scaling of the Permanent Electric Dipole Moment in Isolated Silicon Clusters with Near-Spherical Shape", Phys. Chem. Chem. Phys. 25, 13376-13382 (2023). https://doi.org/10.1039/D3CP00926B

[2] Filip Rivic: "Structure Discrimination and Magnetic Properties of FeSnN with N =8–15" https://www.hkhlr.de/en/projects/2858

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