Size Dependence of FeNC-Model Complexes’ Spectroscopic Parameters

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Clusters
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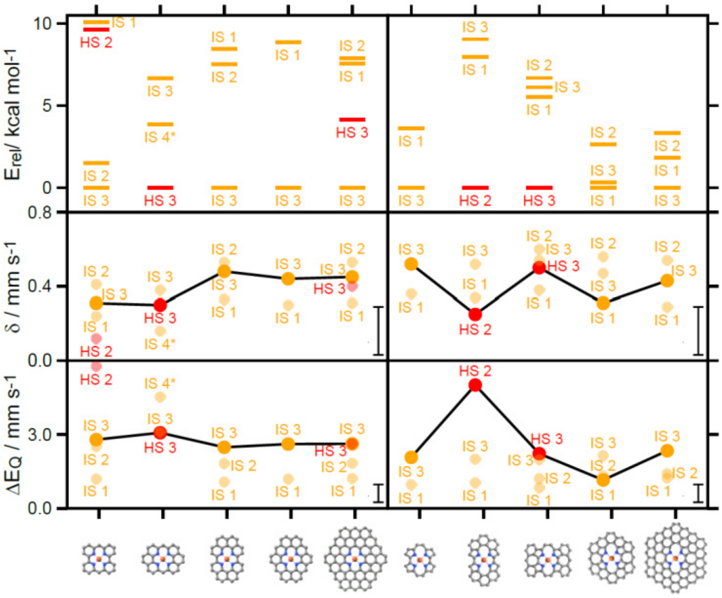

Figure 1: Development of the relative spin state energetics (E_{Rel}) relative to the ground state, and the Mössbauer parameters isomer shift (δ) and quadrupole splitting (ΔE_Q) with an increasing system size of pyridinic (right) and pyrrolic (left) FeNC model complexes. On the x-Axis, the top-view of the models is shown with carbon atoms in grey, nitrogen in blue, iron in orange and hydrogen emitted for clarity. Intermediate spin states (IS) with a total multiplicity 2S+1=3 are shown in yellow, high spin states (HS) with a total multiplicity of 2S+1=5 in red. Spin states with the same occupation of the iron-d-orbitals are given the same number. In the four lower panels, the connected points with solid, large circles correspond to the electronic ground state, the unconnected points with transparent, smaller circles to excited states with relative energies of less than 10 kcal mol^{-1}.

Introduction

While hydrogen is promising for energy storage or mobility applications, the platinum catalysts often needed to convert its chemical energy into electricity hinder its broad application; the noble metal is problematic both economically and ecologically. This motivates the search for alternative catalyst materials, upon which so-called FeNC catalysts, where FeN4 centers are dispersed in graphene-like carbon matrices, aroused the interest of researchers for over a decade. FeNC catalysts have the potential to compete with platinum catalysts in terms of activity and selectivity, but still suffer from stability issues and poor understanding of their catalytic center. The latter is due to a pyrolysis step in their preparation and hence an amorphous structure. This necessitates nuclei specific spectroscopy methods, such as Mössbauer spectroscopy, for investigating the FeN_4 center. Said nuclei specific methods are on their own unable to capture the structural complexity of the FeN_4 center, meaning that they need to be paired with FeNC models for successful structural elucidation. In this project, our group investigated theoretical models for the FeNC catalytic center using quantum chemistry. A key challenge in using theoretical models is the macromolecular graphene-like surface, in which the FeN4 centers are embedded; such macromolecular structures cannot be modeled directly with quantum chemistry. Therefore, models are needed, which can mimic the surface behavior, so that the FeN_4 center experiences similar conditions as in a real surface. One approach is to use molecular models with a sufficiently large π-system, which imitates the expected graphene-like surroundings of the FeN_4 center. Hereby, finding a suitable model size is essential. Models too small do not reproduce the experimental environment. Larger models on the other hand add more computation time to a problem, which is already quantum chemically complicated due to the occurrence of the transition metal iron. We did a systematic size variation of two typical FeNC-models, a phenanthroline-inspired pyridinic model (nitrogen atoms in six-membered rings) and a porphyrin-inspired pyrrolic model (nitrogen atoms in five-membered rings), to find a suitable model size for these molecular models. As many models exceed fifty carbon atoms, the iron nucleus introduces additional complexity, and different spin states need to be viewed, the use of a high-performance cluster was essential for this work.

Methods

All quantum chemical calculations were performed with density functional theory, which connects the electron density of a system to its energy. This method was chosen for its computational efficiency, as high-accuracy wave-function methods, despite desirable due to the models' electronically complex iron nucleus, were not feasible for the system sizes investigated.

Results

Mössbauer parameters and spin state energetics were obtained for two different model types at five different model sizes. It was found that both Mössbauer parameters and electronic ground state converge within the error of the method used at an intermediate model size of 36/50 carbon atoms for the pyridinic/pyrrolic model, corresponding to two carbon full rings around the FeN_4 center (see also Figure 1).

Discussion

It is concluded that molecular FeNC models with two full carbon rings around the FeN_4 center deliver a good tradeoff between accuracy and computational costs. When looking into models not investigated in this work, this is also a good starting point for evaluating a suitable model size. Upon viewing different electronic structures for the same model size, we found it important, to take all probable electronic structures and orbital occupations into account, even if they have the same total multiplicity value. For our relatively planar models, especially the intermediate spin states were low in energy. If states energetically close to the ground state occur, this can hint at a multireference character of the system, which hinders ground state convergence with density functional theory methods. Here, an additional increase of the system size is not sensible, as a multi-reference character cannot be fully resolved with density functional theory in either case.

Publications

Niklas von Rhein: "Computational models for FeNC catalysts: A detailed view on electronic structures from molecular to periodic models", (Tandem-Talk), Understanding Iron and Friends, Darmstadt (Germany), 03.09.-05.09.2024

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