

Computational Study of the Electronic Structure of Co²⁺ Aqua-Complexes

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Transition metal complexes (TMCs) with partially filled *d*-orbitals belong to the most challenging systems to describe with theoretical methods [1,2]. Herein we investigate Co²⁺-complexes with a varying number of aqua ligands and consequently a changing symmetry. The problem is inspired by the nucleation process of zeolitic imidazolate frameworks (ZIFs), where it was shown that the symmetry of the precursors is reduced by ligand elimination and substitution reactions [3]. The octahedral precursors with simple ligands, such as water, methanol, and/or NO₃⁻ are transformed to 5 and finally 4-coordinated complexes with imidazole ligands. This reduction of the symmetry will have a large influence on the electronic structure and more specifically on the *d*-orbital splitting. This, on its turn, will affect the *d-d* electronic excitations which can be followed by using UV-Vis spectroscopy and which can help to unravel the formation process. In this work, we systematically investigate how the lowering of the number of ligands affects the symmetry, the geometry and the electronic structure of Co²⁺-complexes with 6, 5, and 4 aqua ligands.

Therefore, we first resort to qualitative techniques, such as crystal field theory (CFT) and ligand field theory (LFT), which reveal that the orbital splitting is characteristic for the number of ligands. However, as these techniques are not capable of providing quantitative results without the use of experimental input data, we perform various computational calculations based on Density Functional Theory (DFT). Both Unrestricted DFT (UDFT), in which the α - and β -orbitals are treated separately, as Average Of Configuration (AOC), in which the electrons are distributed evenly over the five *d*-orbitals, will be investigated thoroughly. We unravel which technique is the best suited to properly describe the ground state of these systems. Moreover the impact of the precise nature of the transition metal is investigated, as systematic series of V²⁺, Mn²⁺, and Ni²⁺ hexa-aqua-complexes are investigated. In a next step, we examine the excited state properties of these systems by using DFT based techniques, including Time-Dependent DFT (TDDFT) and Ligand Field DFT (LFDFT).

References

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