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Institutsseminar

Spin-States in 3d-Metal Complexes: Challenges for Quantum Chemistry

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Transition metal ions are well known for their ability to stabilize different spinstates in different coordination environments. For some systems, the energy difference between two spin-states is so small, that an external trigger, such as an optical impuls or a change in temperature, is enough to change the minimum energy spin-state. Materials with this property (which predominantly contain a Fe^{2+} center) can easily be envisioned for applications in memory devices or molecular electronics. Unfortunately, the computational investigation of spin-crossover materials is highly demanding. The size of the systems typically allows no treatment beyond density functional theory (DFT), but most DFT functional are strongly biased toward one of the possible spin-states. Calibration of a given functional using a set of complexes with well-established behavior is relatively wide-spread, but suffers both from a lack of transferability and from an unclear separation of thermal, environmental and electronic contributions to the observed free energy differences. Benchmarking of functionals using purely theoretical electronic energy differences circumvents both problems, but comes with its own complication: The quality of the calculated reference values is difficult to access!
While several recent works address this issue, [1–4] it is far from being solved. In a current project, we determine electronic excitation energies of $[MAr_n]^+$ complexes in the gas phase using photodissociation spectroscopy. Using such small, well-defined and highly symmetric molecules will allow for a benchmark of high- and lower-level quantum chemical methods. This will help to provide suitable tools to properly investigate electronically excited states of larger transition metal complexes such as those occurring in spin-crossover materials.

References
[1] Radoń, M. *Phys. Chem. Chem. Phys.* **2019**, 21, 4854–4870.
[2] Drabik, G.; Szklarzewicz, J.; Radoń, M. *Phys. Chem. Chem. Phys.* **2021**, 23, 151–172.
[3] Reimann, M.; Teichmann, E.; Hecht, S.; Kaupp, M. *J. Phys. Chem. Lett.* **2022**, 13, 10882–10888.
[4] Reimann, M.; Kaupp, M. *J. Chem. Theory Comput.* **2023**, 19, 97–108.

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