DFT study of Cobalt-based single-molecule magnet deposition on graphene

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1. Abstract and motivation

- **Single-molecule magnets (SMMs)** are versatile systems that can be integrated into electronic devices by depositing them onto a solid-state material.
- We studied the **adsorption of Co(II)-based SMMs** onto graphene at **density functional theory (DFT)** level, analyzing the adsorption energies, charge transfer, and geometric changes of the systems before and after deposition.
- We calculated the **magnetic properties** (*g*-tensor and spin Hamiltonian terms *E* and *D*) by complete-active space self-consistent field **(CASSCF)**/N-electron valence second-order perturbation theory **(NEVPT2)**.
- Experimental determination of magnetic properties by high-field electron spin resonance **(HF-ESR) spectroscopy**.

2. Methodology

For molecule adsorption:

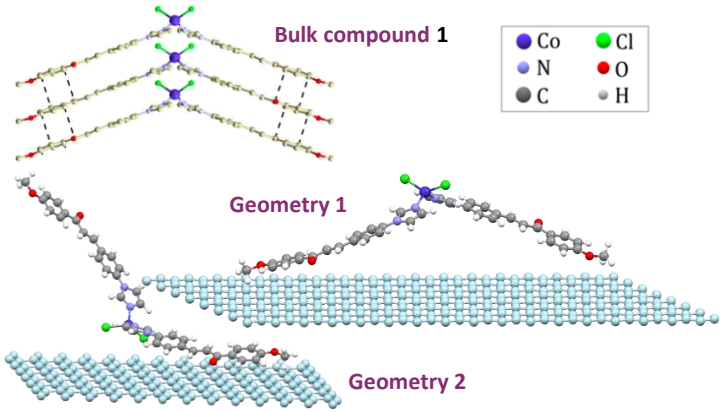
- DFT calculations using the **Vienna Ab-Initio Simulation Package (VASP 5.4.4)**
- Exchange–correlation functional: generalized-gradient approximation (**GGA**) in Perdew–Burke–Ernzerhof (**PBE**) parametrization
- Van der Waals corrections: **D2 method** of Grimme.
- Plane-wave energy cut-off: 420 eV.
- k-space sampling: Γ-centered 2×2×1 Monkhorst–Pack mesh.
- Geometry relaxation criterion: Forces below 0.1 eV/Å

For magnetic properties:

- **CASSCF-NEVPT2** using ORCA 4.2.
- Basis: triple-ζ def2-TZVP (for Co, N, Cl, O), def2-SVP (for C, H).
- Auxiliary basis: def2/J and def2-TZVP/C together with RIJCOSX approximation.
- Active space: five d-orbitals of Co(II) **(CAS(7,5))**.
- *D*- and *g*-tensors: quasi-degenerate perturbation theory (**QDPT**).

3. System

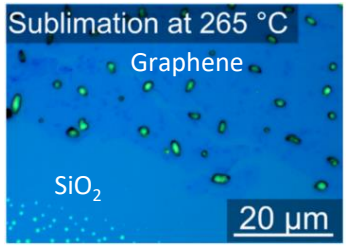
Tetracoordinated Co(II) complex with chalcone ligands on graphene



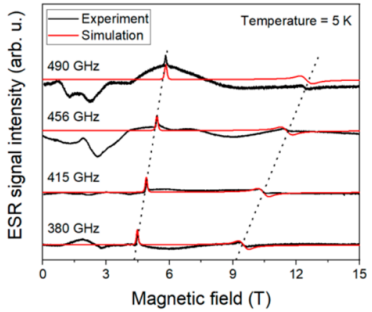
4. Experimental results

- Deposition of the compound showed the formation of nanodroplets for a drop-cast sample and microcrystalites localized at grain boundaries and defects after thermal sublimation.

Optical microscope image



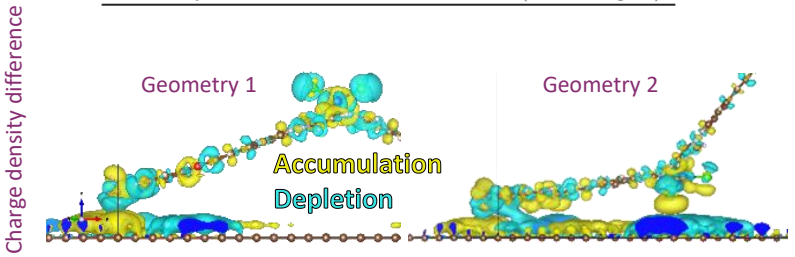
HF-ESR spectra (bulk compound)



5. Theoretical calculations

- Adsorption energy per molecule, equilibrium distance, and charge transfer from Bader analysis.

System	E_{ads} (eV)	d_{eq} (Å)	Δq (e)
Geometry 1	-0.89	3.31	+0.02 (molecule loss)
Geometry 2	-1.08	3.29	-0.005 (molecule gain)



- The spin-Hamiltonian parameters showed fair agreement with HF-ESR experiments on the bulk compound

	D/cm^{-1}	E/D	g_x	g_y	g_z	g_{av}
1	+14.5	0.150	2.325	2.378	2.163	2.289
Geometry 1	+16.4	0.090	2.346	2.364	2.150	2.287
Geometry 2	+17.5	0.132	2.345	2.381	2.143	2.290
HF-ESR	+14.6	0.235	2.320	2.380	2.160	2.287

6. Conclusions and perspectives

- Prediction and characterization of molecular adsorption of a tetracoordinated Co(II) molecule on graphene by DFT, CASSCF-NEVPT2, HF-ESR, XPS, Raman, AFM.
- Ongoing project for theoretical and experimental study of SMMs on surfaces.

Reference

Hrubý, J. *et al.* *Molecules* **25**, 5021 (2020)

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