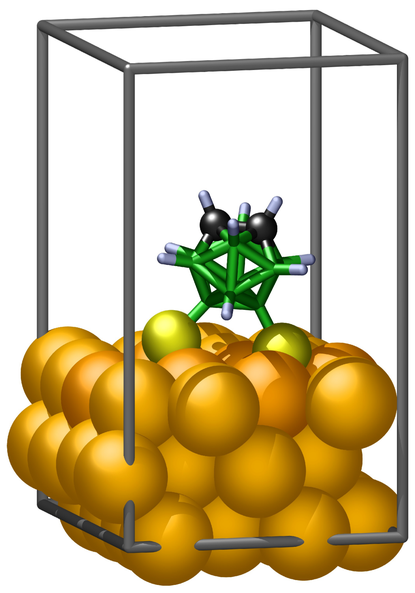
Self-Assembled Monolayers of Polyhedral Dicarbadodecaborane Dithiols: A Computational Assesment of High Coverage Patterns

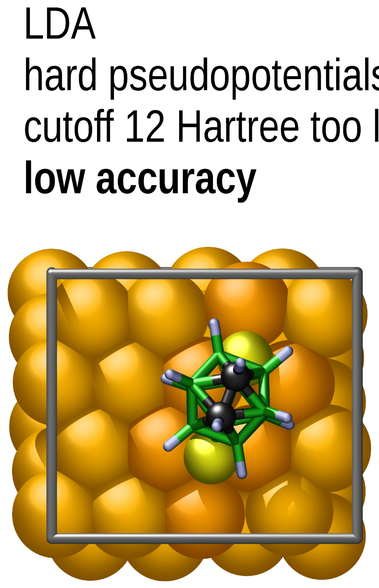
Jan Macháček, jmach@iic.cas.cz
Institute of Inorganic Chemistry of the ASCR, v.v.i., Husinec-Řež 1001,
250 68 Řež, Czech Republic

Introduction

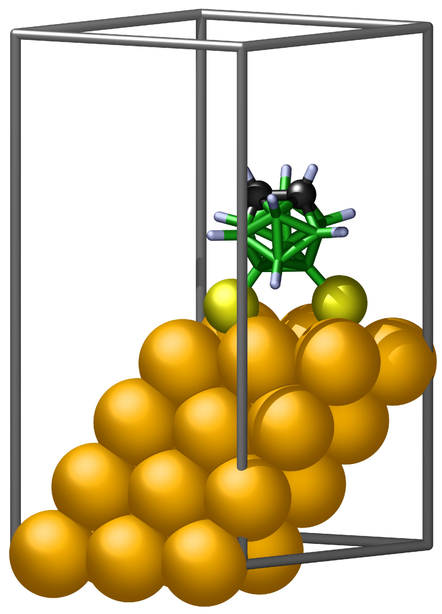
During the last decade, carborane thiols were introduced as building blocks for self-assembled monolayers on metal surfaces.[1][2][3] They form extremely stabe monolayers, especially 9,12-$(HS)_2$-1,2-$C_2B_{10}H_{10}$ surpasses even its 1,2-isomer.[2] To complement experimental studies, the SAMs are modeled by DFT calculations of periodical systems using the Abinit program.[4]



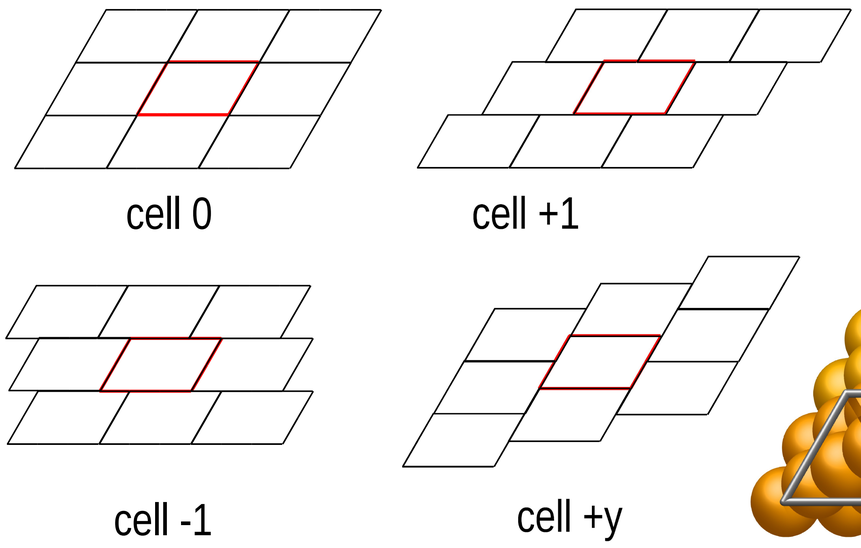
Minimalistic setup:
LDA
hard pseudopotentials (Troullier-Martins)
cutoff 12 Hartree too low
low accuracy



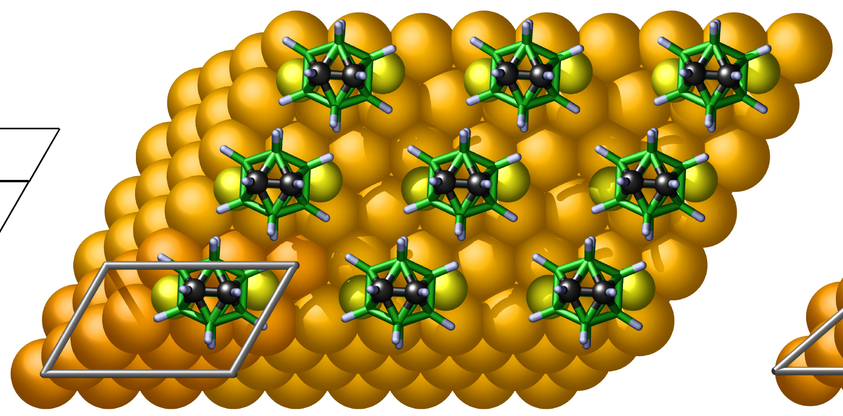
GGA (PBE)
Projector Agmented Waves
double grid cutoffs:
15 Hartree, 30 Hartree
accuracy?



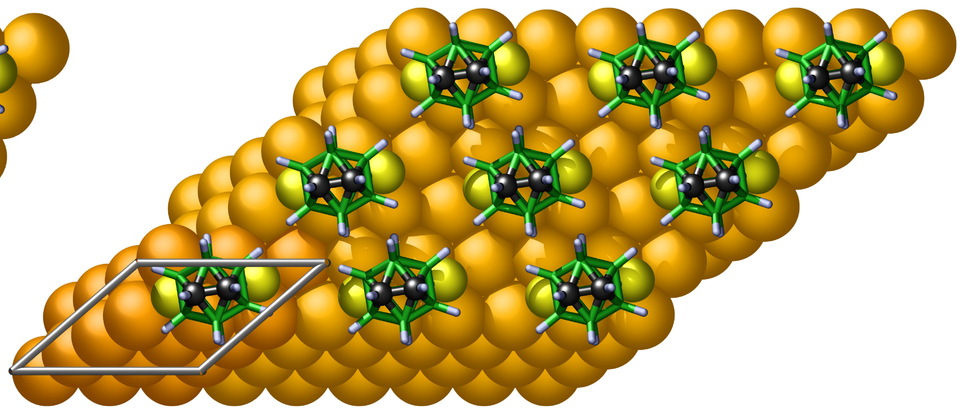
Possible packing:



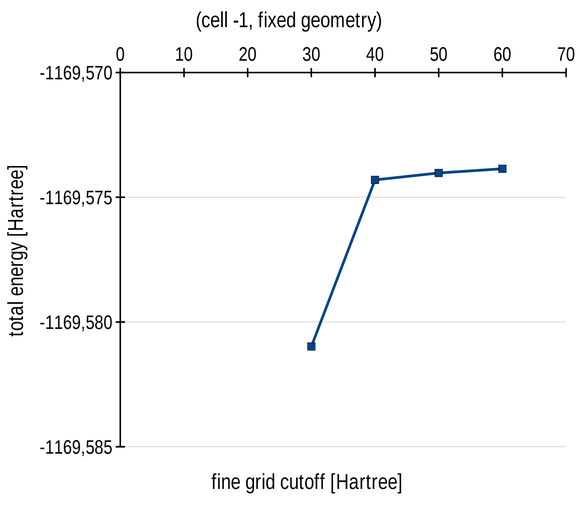
$9,12\text{-}S_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ SAMs

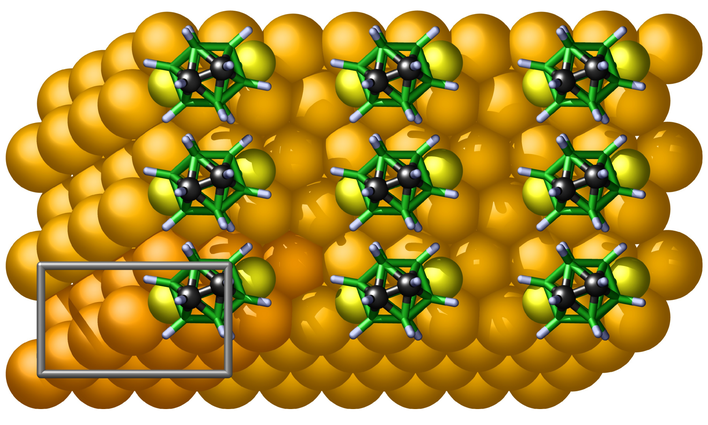


cell 0: -1169.6840 Hartree
ΔE: 17.2 kJ/mol

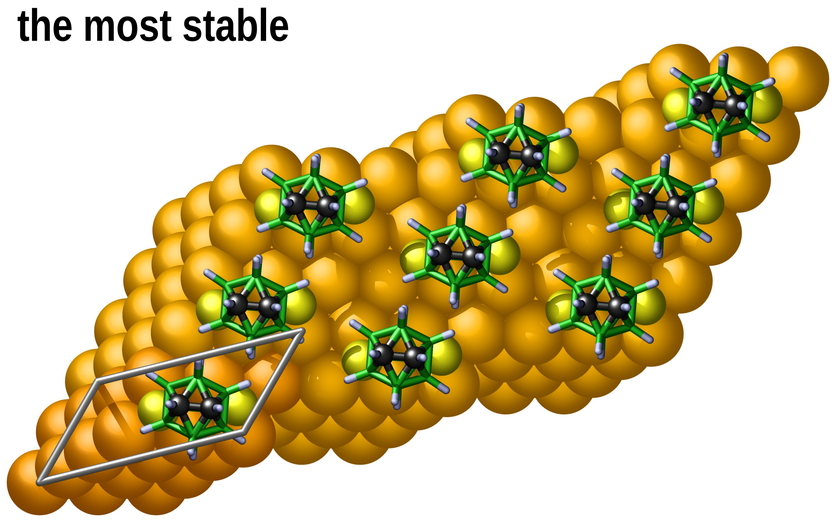


cell +1: -1169.6906 Hartree
the most stable





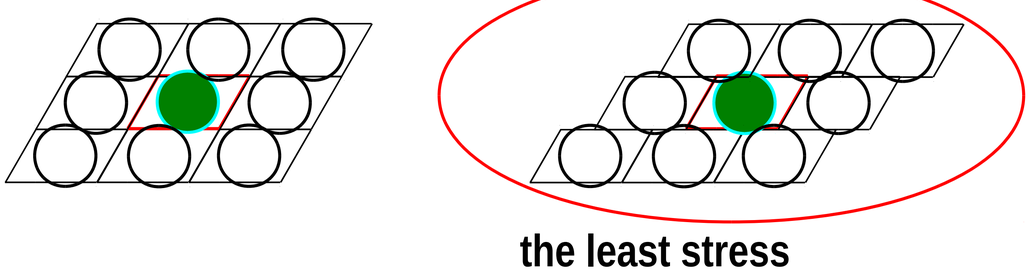
cell -1: -1169.5810 Hartree
ΔE: 287.7 kJ/mol



cell +y: -1169.6843 Hartree
ΔE: 16.5 kJ/mol

The calculations for **$1,2\text{-}S_2\text{-}1,2\text{-}C_2B_{10}H_{10}$** moiety are already under way with the fine grid cutoff 50 Hartree. After a convergence test in the main grid cutoff, all the results will have to be finalised with higher accuracy.

More than simple drawings?



the least stress

Wrong step? Go on:

- complete the **$1,2\text{-}S_2\text{-}1,2\text{-}C_2B_{10}H_{10}$** calculations
- use the first results to set up more accurate calculations
- proceed to calculate observable quantities (beyond drawings)
- explore configurations with gold adatoms at the surface and add them to the comparison

Acknowledgements

The carborane-based SAM survey is led in our institute by Tomáš Baše, to whom I thank for a lot of experimental input and valuable discussion. The work was enabled by the Academy of Sciences of the Czech Republic, Research Plan No. AV0Z40320502, and further sponsored by the Grant Agency of the Academy of Sciences of the Czech Republic, grant numbers IAA400320901, M200320904, and KAN400480701.

References:

[1] T. Base, Z. Bastl, Z. Plzak, T. Grygar, J. Plesek, M. Carr, V. Malina, J. Subrt, J. Bohacek, E. Vecernikova, O. Kriz, Langmuir 21 (2005) 7776-7785.
[2] T. Base, Z. Bastl, V. Havránek, K. Lang, J. Bould, M.G. Londesborough, J. Machácek, J. Plesek, Surface and Coatings Technology 204 (2010) 2639-2646.
[3] J.N. Hohman, S.A. Claridge, M. Kim, P.S. Weiss, Materials Science and Engineering: R: Reports 70 (2010) 188-208.
[5] Abinit, Université Catholique de Louvain, Corning Incorporated, Université de Liège, Commissariat à l'Energie Atomique, Mitsubishi Chemical Corp., Ecole Polytechnique Palaiseau, and other contributors, n.d.