

## Density-functional study of alkyne adsorption on Si(001) and comparison to STM results

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The organic functionalization of semiconductor surfaces is an important task in order to improve upon existing devices (e.g. molecular electronics) in the long-term. To this end, an accurate experimental and theoretical description of promising organic molecules on these surfaces is necessary.[1] In this computational study, we used dispersion-corrected density-functional theory (PBE-D3)[2,3] in order to shed light on the adsorption of acetylene and cyclooctyne on the Si(001)c(4x2) surface. While the adsorption of simple unsaturated molecules like ethylene[4] and acetylene has been thoroughly explored in the past, the smallest cyclic molecule with a carbon-carbon triple-bond — cyclooctyne — and its interactions with this highly relevant surface was not known prior. Starting from a high-resolution STM study of this system by our collaborators in Marburg[5], we explored the adsorption behavior of cyclooctyne from the low to the high coverage regime. The focus of these computational investigations was the explanation of the observed features in the STM pictures.[5] To this end, we conducted STM simulation of the adsorption modes found in the Tersoff-Hamann approximation[6] and were able to shed light on the observed features and could test the experimental hypotheses of possible adsorption modes. We could conclusively explain the adsorption mode of cyclooctyne in agreement with the experimental observations.

- [1] S.F. Bent, *Surface Chemistry in Chemical Bonding at Surfaces and Interfaces* (Eds.: A. Nilsson, L. G. M. Pettersson, J. Norskov), Elsevier, Amsterdam 323 (2007).
- [2] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **132**, 154104 (2010).
- [3] J. Moellmann, S. Ehrlich, R. Tonner, S. Grimme, *J. Phys. Condens. Matter.* **24**, 424206 (2012).
- [4] G. Mette, C. H. Schwalb, M. Dürr, U. Höfer, *Chem. Phys. Lett.* **483**, 209 (2009).
- [5] G. Mette, M. Dürr, R. Bartholomäus, U. Koert, U. Höfer, *Chem. Phys. Lett.* **556**, 70 (2013).
- [6] J. Tersoff, D. R. Hamann, *Phys. Rev. Lett.* **50**, 1998 (1983).