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Nitrogen Adsorption on Graphite: Defying Physisorption

ALEXANDRE TKATCHENKO, MATTHIAS SCHEFFLER, Fritz-Haber-Institut der MPG, Faradayweg 4-6, 14195 Berlin, Germany — The adsorption of a nitrogen molecule at the graphite surface can be considered a paradigm of molecular physisorption [1]. The binding of N_2 can be phenomenologically described in terms of a competition between quadrupole–quadrupole and van der Waals dispersion energies. Of particular interest is the relative stability of the so-called “in-plane”, “out-of-plane” and “pin-wheel” monolayer structures, in which the nitrogen molecules alternate between parallel and perpendicular configurations on the surface. By combining state-of-the-art electronic structure methods, such as dispersion-corrected density-functional theory and Møller-Plesset second-order perturbation theory along with high-level coupled cluster [CCSD(T)] calculations, we are able to gain quantitative insight into the adsorption mechanism of N_2 @graphite and achieve very good agreement with experimental desorption enthalpy. We challenge the commonly held view of a closed-shell adsorbed N_2 molecule, finding a noticeable charge-density polarization for nitrogen in a perpendicular configuration on the surface. We map out the N_2 @graphite potential energy surface as a function of sliding and orientation and discuss the influence of quantum zero-point energy for different adsorption sites. [1] D. Marx and H. Wiechert, *Adv. Chem. Phys.* **95**, 213 (1996).

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