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Quantum chemical calculations on surface adsorption

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For an accurate description of surface reactions, one needs (a) a reliable structure of the surface under reaction conditions, (b) good geometries including the effects of long-range interactions of adsorbed species with the surface, (c) precise adsorption energies, and (d) vibrational frequencies which enable a comparison with experiment. To tackle this, we start from surface structures obtained in VASP calculations, and automatically cut embedded cluster models of different size and shape. Energies are calculated by DFT to investigate cluster size effects and for small clusters by MP2 and CCSD(T) to obtain higher accuracy. In many cases, we are interested in characteristic vibrational frequencies of the adsorbed molecules. Often, we scale DFT calculated harmonic frequencies with a scaling factor obtained for the gas-phase molecule. For benchmark systems, we determine the frequencies directly from ab initio calculations at CCSD(T) level including anharmonic corrections. Results are shown for CO adsorbed on α-Al2O3(0001) [1] and on different low-index CeO2 surfaces [2,3]. Influences of surface termination, coverage, and accuracy of the quantum chemical calculations will be discussed.

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