Understanding the interaction of water with oxide surfaces is of fundamental importance for basic and engineering sciences. Recently, a spontaneous formation of one-dimensional (1D) adsorbed water structures have been observed on CaO(001) [1]. Interestingly, at other alkaline earth metal oxides, in particular MgO(001) and SrO(001), such structures have not been found.

We calculate relative stability of adsorbed water structures on the three oxides using density-functional theory with the hybrid functional HSE06 and ab initio many-body dispersion interaction correction, combined with the ab initio atomistic thermodynamics. Low-energy structures at coverages up to one monolayer are obtained with a first-principles genetic algorithm. Finite-temperature anharmonic vibrational spectra are calculated using ab initio molecular dynamics. We find a range of (T, p) conditions where 1D structures are thermodynamically stable on CaO(001). The orientation and vibrational spectra of the 1D structures are in agreement with the experiments [1]. The formation of the 1D structures is found to be actuated by a symmetry breaking in the adsorbed water tetramer, as well as by a balance between water-water and water-substrate interactions, determined by the lattice constant of the oxide.—