Periodic Calculations

Geometry relaxations of both periodic and isolated systems were performed with the Quantum-Espresso suite of codes[1,2] in the frame of density functional theory with the Kohn-Sham orbitals expanded in plane waves and the effects of atomic core regions accounted for by pseudopotentials.

Ultrasoft pseudopotentials[3] were used throughout the calculations. The exchange–correlation part of the energy functional was modeled with the (spin–unpolarized) generalized gradient approximation (GGA), in the PBE parameterization[4]. Van der Waals interactions were accounted for by use of the vdW-DF functional, available in the Quantum-Espresso suite. The plane wave expansion of the crystalline orbitals was truncated at a cutoff energy of 25 Ry (as determined by convergence of the total energy upon stepwise increase of the cutoff) and a corresponding cutoff of 250 Ry was used for the expansion of the augmentation charge needed by the ultrasoft pseudopotential method.

Due to the large unit cells used for the calculations, the first Brillouin zone was sampled at the gamma point only.

For isolated molecules, a "molecule in the box" methodolgy was applied, where a single molecule is (periodically) simulated in a unit cell which is large enough so as to minimize any interactions between the molecule and its periodic images. Tetragonal unit cells were set up with dimensions large enough to give a minimum separation greater than 10 $\AA$ between nearest atoms of any two contiguous periodic images. The correction of Makov and Payne[5] to the total energy for isolated systems when simulated with large unit cells, as implemented in the Quantum-Espresso suite, was also applied.

For the relaxation of the (**FIXME:**)`4+6@Au` system the "slab method" was used, where an infinite, 2D periodic crystal slab parallel to a given crystallographic family of planes is made periodic along the third space dimension, with the introduction of an additional and sufficiently large vacuum region which ensures that the upper and lower faces of successive slabs do not interact appreciably. FIXME

A gold crystal slab with the open surface parallel to the (111) plane family was set up by periodic repetition of a supercell consisting of 3 layers of Au atoms. A 10 Å thick vacuum region was added along the z axis (normal to the surface). The so prepared crystal slab was relaxed before docking onto it the (previously relaxed) isolated (**FIXME:**)`4+6` molecule and this starting configuration was finally relaxed to convergence. FIXME

During the final structural relaxation of the (**FIXME:**)`4+6@Au` model, the coordinates of the two bottom-most Au layers were freezed at their relaxed values before adsorption and those of the upper-most layer were allowed to vary together with the coordinates of the adsorbed (**FIXME:**)`4+6` molecule. FIXME FIXME

Convergence thresholds for all geometry optimization were 1×10^{-4} Ry for total energy and 1×10^{-3} Ry/Å for the maximum force component acting on atoms.

All simulated models with the corresponding unit cells are shown in figures (**FIXME:** XX). FIXME

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