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Quantum mechanical vs. empirical potential modeling of uranium dioxide (UO_2) surfaces: (111), (110), and (100)

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Abstract

To evaluate the stability, potential reactivity, and relaxation mechanisms on different uraninite surfaces, surface energy values were calculated and structural relaxation was determined for the (111), (110), and (100) crystallographic faces of uranium dioxide (UO_2) using quantum mechanical (density functional theory) and empirical potential computational methods. Quantum mechanical results are compared with empirical potential results, which use surface slab models with two different geometries, as well as various different empirical force fields. The strengths and weaknesses of the different approaches are evaluated, and surface stabilizing mechanisms such as relaxation, charge redistribution, and electronic stabilization are investigated.

Quantum mechanical (q.m.) surface energy results are in agreement with the relative surface energy trends resulting from calculations using three different empirical potential sets for uranium and oxygen (two from Catlow 1977; one from Meis and Gale 1998), and with empirical force-field values published in the literature (Abramowski et al. 1999, 2001). The (111) surface consistently has the lowest surface energy (0.461 J/m^2 from q.m. calculations) and the smallest amount of surface relaxation, followed by the (110) surface (0.846 J/m^2; q.m.), and the (100) surface (1.194 J/m^2; q.m.) (quantum mechanical surface energy values in parentheses are for surface slabs with a thickness of four UO_2 units). Differences exist, however, in the absolute values of surface energies calculated as a function of potential set used. Quantum mechanical values are consistently lower than values calculated using empirical potential methods. A fourth potential set is presented that is derived from fitting electrostatic and short-range repulsive parameters to experimental bulk properties and surface energies and relaxations from quantum mechanical calculations.

Keywords: Uraninite, UO_2, surface energy, quantum mechanical, empirical potentials, force fields, uranium dioxide