Title: A comparison of computational methods for molecular dynamics simulations of ionized fluorocarbon deposition on diamond.

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Mass selective low energy ion bombardment with fluorocarbon cations and radicals is a tremendously useful technique for the precise modification diamond and polymer surfaces. However, the resulting surface chemical processes and their dependence on reaction conditions are not well understood. Ideally, molecular dynamics (MD) simulations may provide critical insight into the atomistic processes that govern these reactions. At the current state of the art, MD simulations of this particular system are limited by the rather long time scales involved in low energy processes. Two approaches that currently may be applied are density functional theory (MD-DFT) with a contracted basis set, as implemented in the SIESTA package, or with a reactive empirical potential such as the Reactive Empirical Bond Order (REBO) potential. In this work, the predictions from MD simulations carried out on the diamond (111) surface with both REBO and SIESTA were tested by comparing calculated reaction enthalpies to higher quality cluster calculations up to the G3MP2 level. The relative error due to basis set superposition and neglect of zero point vibrational contributions in SIESTA were characterized. The comparison showed that such errors, even when minimized through basis set optimization are significant in the SIESTA simulations, but not sufficient to alter qualitative trends in reaction enthalpies. REBO, on the other hand, is limited by its lack of a description for Coulombic interactions, which are shown to strongly influence reactions with ionized species in the low energy regime.