

Towards chemically accuracy for molecule-metal surface reactions: highlights.

Geert-Jan Kroes, Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands

An interesting puzzle consists regarding barrier heights computed with the generalized gradient approximation (GGA) of density functional theory (DFT). With GGA density functionals (DFs), reaction barriers for gas phase reactions are systematically underestimated. However, "tuned" specific reaction parameter (SRP) DFs based on GGA exchange have been shown to describe 10 molecule-metal surface reactions all involving H₂, CH₄, or N₂ with chemical accuracy (1 kcal/mol). At the same time GGA DFs fail spectacularly at describing sticking in systems like O₂ + Al(111). Comparisons to experiments and to first principles diffusion Monte-Carlo (DMC) calculations suggest that GGA DFs work for dissociative chemisorption if (WF-EA) \gtrsim 7 eV, i.e., if the difference of the work function of the metal (WF) and the electron affinity of the molecule (EA) exceeds 7 eV. GGA DFs fail if this difference is smaller than about 7 eV. In the latter case, dynamics calculations on O₂ + Al(111) show that within DFT the solution lies in using higher rung DFs, e.g. screened hybrid DFs. We also show with DMC calculations on H₂ + Al(110) that DFs of various rungs do a remarkably good job of describing how the barrier height to dissociative chemisorption varies with impact site and molecular orientation. Finally, calculations employing orbital dependent friction (ODF) to describe electron-hole pair (ehp) excitation suggest that ehp excitation halves the sticking probability of N₂ on Ru(0001). However, calculations with the local density friction approximation (LDFA) predict a much smaller effect.