Two best-of-both-worlds approaches to dissociative chemisorption on metals

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ABSTRACT

We discuss two approaches to calculating barriers for dissociative chemisorption (DC) on metals. Both use density functional theory, and an exchange-correlation functional with a single adjustable parameter in it. Depending on the work function of the metal surface and the electron affinity of the molecule, the parameter can be adjusted either semi-empirically ("SRP-DFT") [1] or to reproduce a barrier height computed with a first principles method like diffusion Monte-Carlo ("FPB-DFT") [2]. The former approach allows barrier heights to be extracted with chemical accuracy [1], while recent calculations on H_2 + Al(110) (Fig.1) suggest that near-chemical accuracy can be achieved with the latter approach [2] (errors ≤ 1.0 and 1.5 kcal/mol, respectively). The approaches allow one to take advantage of the efficiency of the DFT-world, and the accuracies available through the worlds of experiments and of first principles methods, respectively.

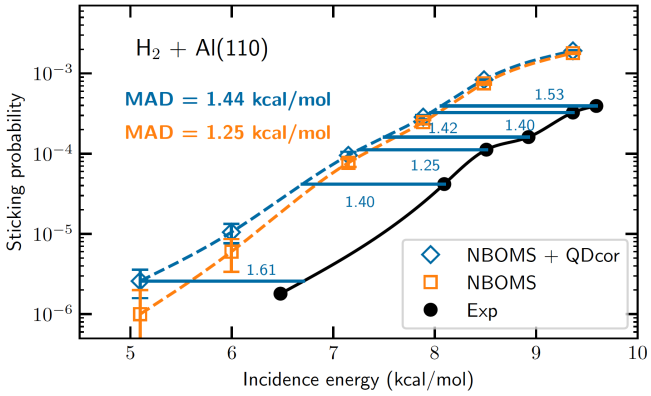

Figure 1: DC probabilities computed using a FPB-DFT potential energy surface with two dynamics approaches (blue and orange symbols, "blue" is best) are compared with results of molecular beam experiments (black symbols).

References

[1] Kroes G.J. Computational approaches to dissociative chemisorption on metals: towards chemical accuracy. *Phys.Chem.Chem.Phys.* **2021**, *23*, 8962-9048.

[2] Powell, A.D; et al. Best-of-both-worlds predictive approach to dissociative chemisorption on metals. *J.Phys.Chem.Lett.* **2024**, *15*, 307-315.