Ab initio molecular dynamics calculations on reactions of molecules with metal surfaces

Nattino, F.

Stellingen

1. Increasing the surface temperature lowers the preference for helicopter-like rotating hydrogen molecules to react on Cu(111). (Chapter 3)

2. The use of functional forms which are more flexible than the traditionally used error function expression helps to improve the quality of the reaction probability curves extracted from associative desorption experiments. (Chapter 4)

3. *Ab initio* molecular dynamics (AIMD) represents a useful tool for studying the dynamics of gas-surface reactions that require the modeling of a large number of degrees of freedom, like methane dissociating on a metal surface, and for testing the accuracy of the underlying potential. (Chapter 5 and Chapter 6)

4. Surface atom motion highly affects the dissociation probability of N_2 on W(110), and should therefore be modeled when testing the accuracy of a density functional or a dynamical model (accounting for electron-hole pair excitation, for instance) for this system. (Chapter 7)

5. The minimum barrier height is an important feature of a potential energy surface (PES), but other characteristics of the PES can also affect the reactivity of a molecule on a surface. (M. Wijzenbroek, and G. J. Kroes, *J. Chem. Phys.* **140**, 084702 (2014))

6. AIMD calculations are computationally expensive compared to PES-based approximate models. However, AIMD allows to test the validity of the dynamical approximations and the basic assumptions on which these models are based without any bias that might result from the fitting of a PES. (B. Jackson, F. Nattino, and G. J. Kroes, *J. Chem. Phys.* **141**, 054102 (2014))

7. Density functional theory at the generalized gradient approximation might not be 'chemically accurate', but it represents an excellent compromise between accuracy and computational cost for describing reactions on metal surfaces.

8. Catalysis does not occur on well-cut defect-free metal surfaces under ultra high vacuum conditions, but catalytic conditions are far from optimal for getting molecular level understanding of the reaction processes.

9. Theoreticians posing new challenges to experimentalists, and experimentalists proving the breakdown of the theoreticians' models help each other in generating new knowledge.

10. Fundamental research has a large return on investment, but low appropriability, especially now that knowledge travels at internet speed. Not adequately funding basic research provokes free rider behavior on the basic research funded by others. However, if no country invests in basic research, there will be no technological progress to gain benefit from. (W. H. Press, *Science* **342**, 817 (2013))