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Photochemistry and spectroscopy of molecules at surfaces: Insights from ab initio molecular dynamics

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The interaction of adsorbates on solid surfaces with light is central to surface spectroscopy, surface photochemistry, and non-adiabatic surface science in general. In the present contribution, light-driven molecular adsorbates will be modelled by ab initio (in one example, semiempirical) molecular dynamics. Three examples will be highlighted:

First, we consider femtosecond laser (FL) pulse driven chemistry at metals, e.g., FL-induced, hot-electron mediated desorption or diffusion. We describe these processes by (Langevin) Ab Initio Molecular Dynamics with Electronic Friction (AIMDEF) based on Density Functional Theory (DFT), and random forces obtained from a two-temperature model. Our focus is on associative desorption of H₂ and isotopomers from Ru(0001) and its “dynamical promotion” [1], as well as on desorption, diffusion and the time-resolved vibrational response of CO on Ru(0001) and Cu(100) [2], respectively.

A second example illustrates how vibrational (IR and Sum Frequency Generation (SFG)) spectra of water-covered aluminum oxide surfaces can be determined with the help of auto- and cross-correlation functions computed from DFT-based AIMD [3].

Third, the step towards explicitly non-adiabatic surface dynamics is taken in the form of semiclassical, AM1/CI-based “surface hopping”. Specifically, we consider cis-trans isomerizations in densely packed, ordered azobenzene layers, and how they are influenced by excitonic and steric effects [4].

- [1] G. Füchsel *et al.*, [Phys. Chem. Chem. Phys. 13, 8659 \(2011\)](#); J.I. Juaristi *et al.*, [Phys. Rev. B 95, 125439 \(2017\)](#).
- [2] R. Scholz *et al.*, [Phys. Rev. B 94, 165447 \(2016\)](#); R. Scholz *et al.*, to be published.
- [3] G. Melani *et al.*, [J. Chem. Phys. 149, 014707 \(2018\)](#).
- [4] E. Titov *et al.*, [J. Phys. Chem. Lett. 7, 3591 \(2016\)](#).