

# Surface Photochemistry from First Principles

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Photodesorption and photodissociation of small molecules adsorbed on surfaces can be regarded as most fundamental processes in surface photochemistry. Despite their apparent simplicity, a microscopic understanding beyond a qualitative picture still poses a true challenge for theory. While the dynamics of nuclear motion can be treated on various levels of sophistication, all approaches suffer from the lack of sufficiently accurate potential energy surfaces, in particular for electronically excited states involved in the desorption or dissociation scenario.

In the last decade, we have developed a systematic and accurate methodology to reliably calculate ground and excited state potential energy surfaces (PES) for different adsorbate-substrate systems<sup>1,2</sup>. These potential energy surfaces serve as a prerequisite for subsequent quantum dynamical wave packet calculations, which allow for a direct simulation of experimentally observable quantities such as velocity distributions. In this talk, I will focus on recent results obtained for photodesorption of NO and CO from a NiO(100) and a TiO<sub>2</sub>(110) surface, respectively<sup>2,4,5</sup>. In contrast to previous studies, we were able to construct highly accurate potential energy surfaces based on correlated quantum chemical calculations (CASPT-2/CCSD(T)). These potential energy surfaces were used in subsequent wave packet studies which reveal new desorption mechanisms<sup>4</sup>. Recently, we extended our studies beyond a static surface wave packet jumping scenario and applied a Surrogate Hamiltonian approach to estimate the resonance lifetime of excited state intermediates by including a bath of electron-hole pairs coupled to the quantum system under investigation. This approach also allows us to treat the system, the bath or both within optimal control theory (OCT) including time-dependent targets. In this talk, I will present recent results and future perspectives<sup>6</sup>.

Furthermore, I will present studies of a prototype photoreaction of a polyatomic molecule on a surface. In particular, the photocatalytic splitting of water on a TiO<sub>2</sub>(110) surface will be investigated for the first time on a high level of theory<sup>3</sup>. A representative potential energy surface (PES) is presented in Figure 1. This reaction might be crucial for the production of solar fuels within a hydrogen based energy economy.

1. T. Klüner, Prog. Surf. Sci. 85, 279 (2010).

2. I. Mehdaoui, D. Kröner, M. Pykavy, H.-J. Freund, T. Klüner, Phys. Chem. Chem. Phys. 8, 1584 (2006).

3. J. Mitschker, T. Klüner, Phys. Chem. Chem. Phys. 17, 268 (2015)

4. I. Mehdaoui, T. Klüner, Phys. Rev. Lett. 98, 037601 (2007).

5. H. Spieker, T. Klüner, Phys. Chem. Chem. Phys. 16, 18743 (2014).

6. E. Asplund, T. Klüner, Phys. Rev. Lett. 106, 140404 (2011).