Photoinduced Dynamics at Surfaces

Thorsten Klüner
Carl-von-Ossietzky Universität Oldenburg, Institut für Reine und Angewandte Chemie,
Carl-von-Ossietzky Str. 9-11, 26129 Oldenburg, Germany
E-mail: Thorsten.Kluener@uni-oldenburg.de

Abstract: Photoinduced desorption of small molecules from oxide surfaces is investigated theoretically. Based on first principles calculations, state-resolved velocity distributions of desorbing molecules could be calculated for several adsorbate/substrate systems. All results were compared to quantum state resolved experiments.

1. Introduction

Photodesorption of small molecules from surfaces is one of the most fundamental processes in surface photochemistry. Despite its 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 scenario.

2. Methodology and Results

In the last decade, we have developed a systematic and accurate methodology to reliably calculate accurate ground and excited state potential energy surfaces (PES) for different adsorbate-substrate systems. 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 contribution, I will focus on recent results obtained for photodesorption of NO and CO from a NiO(100) surface. 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)). Despite the enormous computational cost, this level of theory turns out to be crucial, since less sophisticated approaches such as density functional theory (DFT) cannot even provide a reliable description of ground state properties, not to mention electronically excited states [1].

These potential energy surfaces were used in subsequent wave packet studies which reveal new desorption mechanisms. In the NO/NiO(100) case, we observed an *anti-Antoniewicz* scenario in which the wave packet is initially repelled from the surface but eventually reaches a turning point before it is back-scattered from the surface. State resolved desorption velocity distribution have been calculated, and the results are in good agreement with experimental findings [2].

In the CO/NiO(100) system, we observe the formation of a genuine covalent bond upon photoexcitation for the first time. As demonstrated in the current study, this chemical bond formation is the crucial step in the desorption mechanism for this system [3]. Again, our results are in good agreement with recent experiments.

In addition to the results based on stochastic wave packet calculations based on a jumping wave packet scenario, we performed simulations in which laser excitation of the system and non-adiabatic relaxation are included on microscopic level. Within the framework of a Surrogate Hamiltonian approach [4], we explictly take into account the excitation by ultra-short laser pulses as well the electronic relaxation due to the coupling of the excited intermediate to a bath of electron hole pairs. Additionally, we currently investigate, how the evolution of the wave packet can be modified by control pulses based on optimal control theory [5].

3. References

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