

Introduction

Motivation

Why surface reactions are of general importance

One of the great motivations for studying chemical reactions on surfaces is to gain a detailed understanding about heterogeneous catalytic reactions. About 90% of the chemical manufacturing processes employed worldwide use catalytic methods, most of them heterogeneous catalysis [Cho03]. Among the most prominent reactions is the ammonia synthesis over metal catalysts, responsible for more than 1% of the global energy consumption [Jac00]. Most of the produced ammonia is used for fertilizers, making ammonia indispensable for modern agriculture [Cho03]. Another example illustrating the social relevance of catalysis, is the automotive catalyst where “noxious” exhaust gases are converted to more “benign” chemicals over transition metal surfaces, which reduces automotive pollution.

The increased reactivity of a catalytic process is due to the change of potential energy surfaces (PESs) in the presence of the catalyst. The PES on the catalyst exhibits an energetically more favorable reaction path with lower activation energy. In catalytic surface reactions, the lowering of the reaction barrier originates from chemical bonding of the involved molecules to the substrate. The intramolecular bond strength is weakened or even broken upon adsorption so that the subsequent reactions proceed more easily. In the case of ammonia synthesis ($\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$), this can be envisioned as the energetically very unfavorable dissociation of gaseous H_2 and N_2 , whereas dissociation upon adsorption on a suited catalytic surface is energetically favored.

The lowering of the activation energy increases drastically the reaction rate, whereby the remaining *rate-limiting* step in the majority of heterogeneous catalytic processes is the dissociative adsorption of the educts on a metal surface [Kol02]. This reveals the fundamental importance of the investigation of dissociation and its time-reversed process of association of molecular bonds at surfaces.

Why femtosecond laser excitation is special

The potential energy surfaces quantifying the forces between the atoms involved in a reaction are usually derived under the assumption that the electrons follow the nuclear motion of the atoms instantaneously. This is named the *adiabatic* or Born-Oppenheimer approximation (BOA) [Bor27]. Thereby, *non-adiabatic* coupling effects between nuclear motions and electronic degrees of freedom are neglected. This, however, is only valid as long as the involved PESs do not approach each other significantly. At metal surfaces, where a whole

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manifold of PESs exists, which are coupled by a continuum of electron-hole pair excitations, non-adiabatic coupling between electronic and nuclear degrees of freedom becomes relevant. Thus, the applicability of the BOA to chemical reactions at metal surfaces is a topic of intense debate.

Direct evidence for non-adiabatic effects on molecule-surface interaction comes from experiments showing ejection of electrons from low work function metal surfaces accompanying scattering of highly vibrationally excited molecules [Whi05]. Moreover, the excitation of electron-hole pairs has been observed during adsorption of gases on thin metal films by detection of chemicurrents [Ger01]. The time-reversed process, namely non-adiabatic desorption due to electron-hole pair excitation of the substrate, can not be distinguished from an adiabatic, phonon mediated desorption mechanism with experiments, where the electron and phonon heat bath of the substrate are in equilibrium. Absorption of a femtosecond (fs) light pulse by a metal substrate, however, generates a transient non-equilibrium distribution of hot electrons, which thermalize by ultrafast electron-electron scattering leading to an electron temperature exceeding the lattice temperature by several thousand degrees Kelvin on a sub-picosecond timescale [Lis04]. Coupling of this hot electrons to the adsorbates can cause *non-adiabatic* processes like desorption of molecularly bound species [Bud91, Mis94] or reactions between coadsorbed atomic or molecular reactants [Kao93b, Her98, Bon00a, Den04]. Thus, fs-laser excitation offers the possibility to gain knowledge about electronic contributions in surface reactions. For example, in the case of fs-laser induced CO oxidation on Ru(001), it was shown that hot electron mediated activation of coadsorbed atomic oxygen can induce a chemical reaction which is not accessible under equilibrium conditions [Bon00a]. This means that the reaction path for CO oxidation is "switched on" only due to fs-laser excitation of the substrate.

The elementary steps of chemical reactions itself occur on a femtosecond timescale. The dynamics of a chemical reaction are governed by the traverse of the transition state of the activated complex, which is the "transient structure" that "persists" while old bonds are breaking and new bonds are forming. The transition state theory developed independently by Eyring [Eyr35] as well as Evans and Polanyi [Eva35] predicts that the timescale of the traverse is related to molecular vibrations with a period of typical 100 femtoseconds.

An essential point for the observation of transient processes in the time domain is the determination of an exact starting point. If one wants to study the evolution of a chemical reaction it must be possible to induce and to probe the reaction in a well-defined manner. This is possible with fs-laser pulses which are short compared to the process under investigation which is the basic idea of *femtochemistry*.

In 1999, Ahmed H. Zewail received the Nobel Prize in Chemistry for his pioneering work in this field of understanding and even control of chemical reactions in the gas and solution phase [Zew94]. However, a comparable level of sophistication in the analysis of chemical reactions at surfaces has not been achieved up to now due to the additional complexity of energy dissipation channels introduced by the presence of the substrate interacting with the reactants. Very recently, a direct observation of the time evolution of the lateral motion of a molecule on a surface was presented [Bac05]. The lateral motion of an adsorbate is the most elementary reaction taking place on a surface and is the primary way for adsorbates to meet a reaction partner. However, no intramolecular bonds of the adsorbate are formed or broken. Thus, the real-time observation of molecular bond formation between adsorbates on a surface

remains an open challenge.

Summarizing, one can state that fs-laser excitation is required to determine directly the strength of non-adiabatic contributions in surface reactions on metal substrates. Furthermore, ultrashort laser pulses are required to investigate chemical reactions directly in the time-domain what is still an open challenge concerning the dissociation and association of adsorbates on surfaces.

Why state- and time-resolved investigations are required

One approach to gain microscopic understanding of a reaction is to measure how the energy released during reaction is disposed in the products. The energy partitioning into different coordinates depends in an adiabatic process on the location of the transition state and the shape of the multi-dimensional potential energy surface [Eyr31]. In addition, the energy partitioning can be drastically altered, if non-adiabatic coupling contributes to the reaction [Lun05]. Non-adiabatic friction coefficients exhibit the same dimensionality as the reaction process. Therefore, anisotropic frictional coupling can lead to unequal energy transfer into the different coordinates. This means that the energy content in different degrees of freedom of the reaction product can represent both, *adiabatic* and *non-adiabatic* contributions. *State-resolved* detection of the reaction product is thus required to investigate the *multi-dimensional* character of chemical reactions. Although a direct interpretation of the obtained state-specific data is often not unambiguously possible due to the complexity of the underlying process, the experimental data represent a benchmark for theory to reproduce and quantify the observed phenomena.

To reveal experimentally the non-adiabatic coupling strength which has to be considered in the fs-laser induced activation of a surface reaction, time-resolved experiments are required. To investigate if the reaction rate is significantly enhanced due to non-adiabatic coupling to the hot electrons, one performs a so-called two-pulse correlation measurement. In this experimental scheme, two laser pulses are delayed in time. For time delays shorter than the electron-phonon equilibration time, very high electron temperatures are achieved since the second pulse additionally heats the hot electron distribution induced by the first pulse. Time delays larger than the electron phonon equilibration times result in lower electron temperatures, since the second pulse does not benefit from excitation of the first pulse any more. This means that varying the time delay of the two pulses in a certain time regime allows to vary the electron temperature, whereas the phonon temperature remains almost constant. Since the adsorbate-substrate coupling is temperature-dependent, one has the possibility to investigate adiabatic and non-adiabatic contributions to the reaction rate.

Investigated systems

The substrate: Ru(001)

In the present thesis, associative desorption from a Ru(001) surface was investigated. In catalysis, the surface structure and composition is empirically optimized aiming at best catalytic properties which often results in complex surfaces. For an understanding of the elementary

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processes and reaction mechanisms, such surfaces are not well suited. In fundamental research, one is interested in a reduction of the relevant degrees of freedom so that an exact characterization of the system under investigation is possible. Thus, single crystal surfaces are considered as important model catalysts. Transition metal surfaces exhibit a high catalytic reactivity due to high density of states of the partially filled d-bands at the Fermi level [Sch00]. Concerning the ammonia synthesis, traditionally an iron catalyst is used [Hab05, Seh99], but recently ruthenium based catalysts have attracted a great deal of attention, as potentially better catalysts for industrial ammonia production [Dah98, Dah00a]. This allows to designate the single crystal Ru(001) surface used in the present experiments as a well suited candidate for the investigations of catalytic relevant surface reactions.



Although the dissociation of hydrogen is mostly not the rate determining step in catalytic reactions, it is important to have a detailed understanding of this reaction because of its model character. The recombination of two atomically bound hydrogen atoms on a Ru(001) surface, which form a hydrogen molecule and leave the metal substrate, acts as a prototype of a surface reaction, since it is one of the simplest surface reactions one can think of.

Very recently, the fs-laser induced associative desorption of hydrogen from Ru(001) was investigated and a purely electron mediated reaction mechanism revealed [Den03b, Den04]. However, only little is known about the energy partitioning during the reaction. Earlier measurements show that fs-laser induced reaction releases the nascent H_2 molecules from the surface with very high translational energy [Den03b]. The energy content in internal degrees of freedom, namely vibrational and rotational, still remained unknown. Hence, the energy partitioning in the fs-laser induced associative hydrogen desorption from Ru(001) is investigated and compared with the outcome of *ab initio* non-adiabatic molecular dynamic calculation performed by Luntz and coworkers [Lun06]. Detailed understanding of adiabatic and non-adiabatic contributions to the fs-laser induced hydrogen recombination are obtained.



The similarity of potential energy surface topologies for activated dissociation of π -bonded molecules on transition metals [Mav99, Ham00a] allows to compare the CO formation on Ru(001) with the catalytically very relevant $\text{N}_2/\text{Ru}(001)$ system which is a topic of intense debate concerning the applicability of an adiabatic description to the reaction dynamics. For $\text{N}_2/\text{Ru}(001)$, experimental findings for the thermal associative desorption of N_2 from Ru(001) can not be theoretically reproduced considering a purely adiabatic reaction mechanism [Lun05], whereas the dissociative adsorption is adiabatically well described if the full dimensionality of the N_2 molecule is considered [Día06a, Día06b]. Calculated non-adiabatic coupling strengths for $\text{N}_2/\text{Ru}(001)$ are almost one order of magnitude larger than those found for the H_2 recombination [Lun05, Lun06]. Such large non-adiabatic contributions are also expected to contribute to the associative desorption of CO from Ru(001) what can be investigated via fs-laser induced desorption.

Beside the determination of possible non-adiabatic contributions to the reaction mechanism, the association of CO on Ru(001) might be suited to measure directly the temporal evolution

of the bond formation by probing the internal CO stretch vibration time-resolved in pump-probe experiment.

Outline of this thesis

In Chapter 1, the theoretical concepts concerning surface reactions, their adiabatic and non-adiabatic description, the response of a metal substrate to fs-laser excitation and adsorbate-substrate coupling are discussed in detail.

The experimental setup required to investigate the fs-laser induced associative desorption time- and state-resolved is described in Chapter 2.

In Chapter 3, the results obtained for the state-resolved detection of fs-laser induced hydrogen desorption from Ru(001) are presented and compared to first principle molecular dynamic calculations performed by Luntz et al. [Lun06]. The theoretical approach of these calculations is explained in Appendix A.

The investigations concerning the reaction mechanisms of the fs-laser induced CO recombination are shown in Chapter 4. Unfortunately, the time-resolved investigation of the CO bond formation by vibrational SFG spectroscopy was not feasible due to insufficient sensitivity and an estimation of the required data acquisition time is given in Appendix B.

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