Summary

The present thesis investigates the energy transfer mechanisms in surface reactions. This is of fundamental importance for the microscopic understanding of the elementary steps of heterogeneous catalysis. Since the dynamics occur on an ultrafast timescale, fs-laser pulses are adequate to characterize the energy transfer mechanisms between adsorbate and substrate. Contributions from multi-dimensional dynamics are examined by state-resolved detection of the reaction products. The catalytic relevant associative desorption of H_2 (D_2) and CO from a Ru(001) surface have been investigated.

A recent topic of intense debate is the applicability of the Born-Oppenheimer approximation for the theoretical description of reactions on metal surfaces. This approximation does not take into account excitation of the substrate electrons and is thus denoted as *adiabatic*. Femtosecond-laser excitation of the metal substrate is well-suited to investigate the strength of *non-adiabatic* coupling between metal substrate and adsorbate. The non-equilibrium of highly excited electrons and "cold" phonons after fs-laser excitation allows to separate adsorbate coupling to substrate electrons and phonons.

The obtained experimental data is modeled within the framework of the two-temperature-model (2TM), describing the temporal evolution of the electron and phonon heat baths of the metal substrate after excitation with fs-laser pulses, and a frictional approach for the adsorbate substrate interaction. That allows to specify adiabatic and non-adiabatic coupling strengths contributing to the reaction mechanism under investigation.

Associative desorption: $\mathbf{H_{ads} + H_{ads} \xrightarrow{\text{fs-laser}} H_{2,gas}}$

Recent investigations in our group have revealed that the fs-laser induced associative desorption of H_2 (D_2) from Ru(001) is initiated on an ultrafast timescale and clearly activated by non-adiabatic coupling [Den03b, Den04]. Frictional coupling coefficients of $\eta_{el,H_2} = 2 \cdot \eta_{el,D_2} = 1/180\,fs^{-1}$ have been determined [Den03b]. To gain further microscopic understanding of this reaction, the energy release during desorption into the desorbing molecules is analyzed, i.e. the partitioning of the energy release into different molecular degrees of freedom is determined.

The mean translational energy of the desorbing hydrogen molecules has been determined via time-of-flight (TOF) measurements. With increasing absorbed laser fluence, the translational energy $\langle E_{trans} \rangle$ increases as well. Translational temperatures $T_{trans} = \langle E_{trans} \rangle / 2k_B$ ranging from 2000 to 3000 K and from 3000 to 4000 K for desorbing D_2 and H_2, respectively, are measured. This pronounced isotope effect and the fluence dependence are qualitatively well reproduced within the framework of the applied friction model. The modeled adsorbate temperatures T_{ads} are a factor 1.4 lower than the translational temperatures T_{trans}.

Summary

The energy transfer to the internal molecular degrees of freedom, i.e. the rotation and vibration, is determined via state-resolved detection of the desorbing molecules. This is done by applying resonance enhanced multi-photon ionization (REMPI) of the desorbing D_2 molecules. Therefore, a tunable vacuum-ultraviolet laser system synchronized to the reaction inducing fs-laser system has been installed. The measured rovibrational state distribution for D_2 desorbing from Ru(001) after fs-laser excitation with $85\,\mathrm{J/m^2}$ absorbed fluence exhibits non-thermal behavior, i.e. can not be described by a single Boltzmann distributions. Instead, the sum of two Boltzmann distributions, characterized by two temperatures, $T_1 = 800\,\mathrm{K}$ and $T_1 = 1530\,\mathrm{K}$, reproduces the experimental data. Thus, a mean rotational temperature of $T_{\mathrm{rot}} = 910\,\mathrm{K}$ and a mean vibrational temperature of $T_{\mathrm{vib}} = 1200\,\mathrm{K}$ can be derived, representing the energy content $\langle E \rangle = k_{\mathrm{B}}T$ in the corresponding molecular degree of freedom.

The molecular alignment of the desorbing D_2 does not show a dependence on rovibrational state nor on the absorbed laser fluence. Nevertheless, a significant positive alignment is found which implies that the desorption process leads mainly to helicopter-like rotation of the desorbing molecules.

The observed unequal energy partitioning can be described by the ratio of translational, vibrational and rotational temperatures representing the energy content in the corresponding degree of freedom and is determined to be 2.7:1.3:1, i.e. there is a preferential energy transfer into the translational coordinate. The overall energy content in the desorbing particle flux is well reproduced by the applied one-dimensional friction model, however the origin of the unequal energy partitioning can not be identified by such a 1D approach. Unequal energy partitioning can either be due to the topology of the *adiabatic* multi-dimensional potential energy surface or due to anisotropic *non-adiabatic* coupling, leading to differences in energy transfer to the different molecular degrees of freedom.

Multidimensional "first-principle" trajectory calculations considering non-adiabatic coupling performed by Luntz et al. [Lun06] reveal that the unequal energy partitioning is due to the existence of a translational barrier on the adiabatic ground state potential energy surface. Inspection of the calculated trajectories shows that the successful description of the multidimensional hydrogen recombination via a one-dimensional friction model is based on rapid intermixing of the molecular coordinates during desorption.

Associative desorption: $\mathbf{C}_{\mathrm{ads}} + \mathbf{O}_{\mathrm{ads}} \xrightarrow{\text{fs-laser}} \mathbf{CO}_{\mathrm{gas}}$

The fs-laser induced associative desorption of CO from Ru(001) is found to originate predominantly from oxidation of isolated atomically "reactive" carbon atoms, whereas oxidation of surface carbon exhibiting carbon-carbon bonds is not observed. Although associative desorption is considered to be a second order process, the C oxidation under the experimental conditions is determined to be of pseudo first order due to the excess of oxygen atoms.

A non-linear dependence of the reaction yield Y on the absorbed laser fluence $\langle F \rangle$ is found according to $Y \propto \langle F \rangle^n$ with $n \approx 4$ for excitation with 400 and 800 nm light. The decay of the reaction rate within a series of exciting laser pulses allows to determine an effective reaction cross sections σ_{eff} and the desorption probabilities P_{des} for both wavelengths. An absorbed fluence of $\langle F \rangle = 170\,\mathrm{J/m^2}$ results in $\sigma_{\mathrm{eff}} = 4.9 \cdot 10^{-18}\,\mathrm{cm^2}$, $P_{\mathrm{des}} = 0.07$ and $\sigma_{\mathrm{eff}} = 1.1 \cdot 10^{-18}\,\mathrm{cm^2}$, $P_{\mathrm{des}} = 0.03$ for excitation with 400 nm and 800 nm light, respectively. The factor 2.5 higher

reaction yield obtained for excitation with 400 instead of 800 nm light can be attributed to the shorter optical penetration of 400 nm light in Ru(001) leading to higher surface temperatures for the same amount of absorbed energy. No indication for a contribution of non-thermalized hot electrons to the wavelength dependence is found.

The reaction mechanism of the fs-laser induced CO recombination is furthermore investigated with a two-pulse-correlation (2PC) measurement which exhibits a FWHM of ≈ 20 ps. Thus, the reaction is not purely mediated by ultrafast electronic coupling. Qualitative and quantitative successful modeling of the experimental data reveals that the reaction is mediated by electrons *and* phonons. The electronic, i.e. non-adiabatic, contribution is responsible for an ultrafast activation of the reaction which is modeled to occur within ≈ 1 ps after excitation. Thus, one has to be careful in contributing 2PC widths larger than several picoseconds automatically to slow, purely phonon mediated reaction mechanisms. A non-adiabatic coupling constant of $\eta_{\mathrm{el}} = 1/500\,\mathrm{fs}^{-1}$ is of the same order of magnitude as those found for H_2/Ru(001) which requires to take into account a mass-independent electronic coupling strength which is one order of magnitude larger in the present case. This is in good agreement with calculated coupling strengths for the related system N_2/Ru(001) system.

The energy transfer to the nuclear degrees of freedom during the desorption process is investigated concerning the translation perpendicular to Ru(001) surface. Translational energies expressed by a translational temperature $T_{\mathrm{trans}} = \langle E_{\mathrm{trans}} \rangle / 2k_{\mathrm{B}} \approx 700\,\mathrm{K}$ exhibit only weak dependence on the absorbed laser fluence and are a factor 2 to 3 lower than the surface temperatures present after fs-laser excitation. The origin of this deviation can either be due to unequal energy partitioning between the molecular degrees of freedom or non-adiabatic damping, but remains speculative as long as the energy content of the internal molecular degrees of freedom is unknown.

Unfortunately, the real-time observation of the transient formation of the intramolecular CO stretch vibration via time-resolved vibrational SFG spectroscopy was not successful because of a too low SFG signal strength.

Conclusions

In summary, it is found that *non-adiabatic* electronic coupling is dominating the activation of both investigated fs-laser induced associative desorption processes. One order of magnitude larger *non-adiabatic* electronic coupling strengths are found for the CO recombination compared to the hydrogen case. The energy partitioning in the associative desorption of hydrogen is governed by the topology of the *adiabatic* ground state potential energy surface. The combination of experimental and theoretical investigations reveals an microscopic understanding of the fs-laser induced associative hydrogen desorption.