State- and Time-Resolved Investigations of Energy Transfer Mechanisms in Femtosecond-Laser Induced Associative Desorption

Im Fachbereich Physik
der Freien Universität Berlin
eingereichte Dissertation

Steffen Wagner

Oktober 2006

Diese Arbeit entstand in der Arbeitsgruppe von
Prof. Dr. Martin Wolf an der Freien Universität Berlin.

Berlin, im Oktober 2006

Erstgutachter:	Prof. Dr. Martin Wolf
Zweitgutachter:	Prof. Dr. Karl-Heinz Rieder
Tag der Disputation:	21. November 2006

"Sicherheit?! - Ich kann Dir eines mit Sicherheit sagen:
Am Ende Deines Lebens wirst Du tot sein."

Martin Wolf, Februar 2003

Entgegnung auf den Einwand, die Erfolgsaussichten des REMPI-Experiments seien unsicher

Abstract

This thesis investigates the reaction mechanisms of femtosecond-laser induced associative desorption from metal surfaces. The energy transfer between a metal substrate and an adsorbate occurs on an femtosecond (fs) timescale, mediated by coupling to the phonons and the electrons. The potential energy surfaces quantifying the forces between the atoms involved in a reaction are usually derived under the assumption that the electrons follow instantaneously the nuclear motion of the atoms. This is named the *adiabatic* or Born-Oppenheimer approximation. Thereby, *non-adiabatic* coupling effects between nuclear motions and electronic degrees of freedom are neglected. The applicability of the Born-Oppenheimer approximation to reactions on metal surfaces is a topic of intense debate, due to the possibility of low-energetic electron-hole pair excitations in the metal substrate. The importance of non-adiabatic, i.e. electronic, contributions are studied with fs-laser pulses exploiting the strong non-equilibrium between electrons and phonons directly after excitation.

In this thesis, the fs-laser induced reactions $H_{ads}+H_{ads} \rightarrow H_{2,gas}$ and $C_{ads}+O_{ads} \rightarrow CO_{gas}$ on Ru(001) are examined. The analysis of the experimental data is based on the two-temperature model, describing the temporal evolution of the electron and phonon temperatures after excitation by fs-laser pulses, and frictional coupling between adsorbate and substrate.

For the purely electron mediated ultrafast hydrogen recombination the energy transfer to different degrees of freedom of the desorbing molecule has been examined by performing resonance enhanced multiphoton ionization (REMPI) and time-of-flight (TOF) measurements. Unequal energy partitioning is found with a ratio of 2.7:1.3:1 for translational, vibrational and rotational energies expressed in terms of the corresponding temperatures.
Ab initio molecular dynamic calculations considering electronic coupling performed by Luntz et al. [Lun06] reveal that the energy partitioning is due to the topology of the adiabatic potential energy surface and not due to anisotropic electronic coupling.

The associative desorption of CO is found to be driven by both substrate electrons and phonons which results in an ultrafast reaction mechanism although the width of the measured two-pulse correlation is ≈ 20 ps, which is usually interpreted as evidence for purely phonon mediated reactions. The determined electronic coupling strength is comparable with theoretical predictions for related systems and one order of magnitude larger than for H_2/Ru(001). Excitation with 400 nm instead of 800 nm light enhances the reaction rate, an effect which is due to the shorter optical penetration depth for 400 nm light causing higher surface temperatures. The translational energy of the desorbing CO is found to be lower than expected for desorption under equilibrium conditions which might be due non-adiabatic damping or unequal energy partitioning.

In summary, it is found that non-adiabatic electronic coupling is dominating the activation of both investigated recombination processes. The energy partitioning in the associative desorption of hydrogen is governed by the topology of the adiabatic ground state.

Contents

List of Figures

Frequently Used Abbreviations

1D	one dimensional
2D	two dimensional
2PC	2-pulse correlation
2TM	2-temperature model
3D	three dimensional
6D	six dimensional
BBO	β-BaB_2O_4
BOA	Born-Oppenheimer approximation
CCD	charge coupled device
COM	center-of-mass
CPA	chirped pulse amplification
DFG	difference frequency mixing
g DFT	density functional theory
DIET	desorption induced by electronic transitions
DIMET	desorption induced by multiple electronic transitions
ESD	electron stimulated desorption
FSY	first shot yield
FWHM	full width at half maximum
HOMO	highest occupied molecular orbital
IR	infrared
LUMO	lowest unoccupied molecular orbital
MCP	multi-channel plate
MGR	Menzel-Gomer-Redhead
ML	mono layer
OPA	optical parametric amplification
PES	potential energy surface
QMS	quadrupole mass spectrometer
REMPI	resonance enhanced multi-photon ionization
RGA	regenerative amplifier
SHG	second harmonic generation
SFG	sum frequency generation
TDS	thermal desorption spectroscopy resp. spectrum
TFP	thin film polarizer
TPD	temperature-programmed desorption
TPO	temperature-programmed oxidation
TOA	time-of-arrival
TOF	time-of-flight

TST	transition state theory
UHV	ultra-high vacuum
UV	ultraviolet
VUV	vacuum ultraviolet
YWF	yield-weighted fluence