State-selective detection of fs-laser induced D_2 desorption from D/Ru(001)

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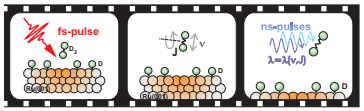
MOTIVATION: GAS-SURFACE DYNAMICS

ABSTRACT

The dynamics of energy transfer processes at surfaces are of fundamental importance for a microscopic understanding of chemical reactions at solid surfaces, e.g. in catalysis. In conventional „thermal" chemistry no distinction between electron- and phonon-mediated reaction pathways is possible, since electrons and phonons are always in thermal equilibrium. However, the transient non-equilibrium between electrons and phonons created by a laser pulse shorter than the timescale of electron-phonon-coupling (typically a few ps in metals) allows for the analysis of the two different processes.

Femtosecond-laser excitation induces recombinative desorption of molecular D_2 from atomic deuterium on a ruthenium surface. Previous work revealed that this reaction is mediated by an non-adiabatic coupling between the laser-excited hot substrate electrons and the nuclear degrees of freedom of the adsorbate [1,2]. Here, we investigate the amount of energy coupled to the different molecular degrees of freedom during desorption. We use resonantly enhanced two-photon ionization (REMPI) to state-resolve the rotational and vibrational distribution of the reaction products. Time of flight (TOF) measurements are perormed to obtain the energy content of the translational degrees of freedom. The rotational and vibrational temperatures (T_{rot}=1200 K and $T_{vib}(v=0)$=800 K, $T_{vib}(v=1)$=1500 K, respectively) extracted out of the state distribution of the desorbing D_2 molecules yield the same order of magnitude as the translational temperature (T_{trans}=2500 K). An observed fluence dependence on the translational temperatures can be qualitatively explained by the electronic friction model, which also accounts for a simple energy balance.



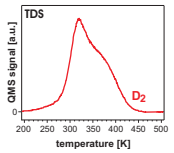
THE SYSTEM D/RU(001)

- H/Ru(001) simple model system.
- Prototype for the investigation of recombinative desorption

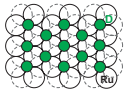
➡ What happens with fs-laser excitation?

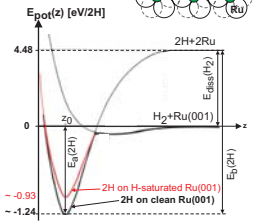
➡ Analysis of energy transfer processes possible?

➡ Differences to thermal desorption?



D/Ru(001):
Saturation structure: 1ML
1x1 - fcc @ <200K

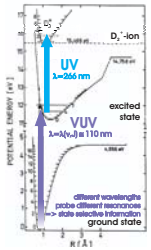




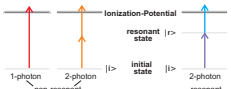
EXPERIMENTAL SETUP

STATE-RESOLVED DETECTION

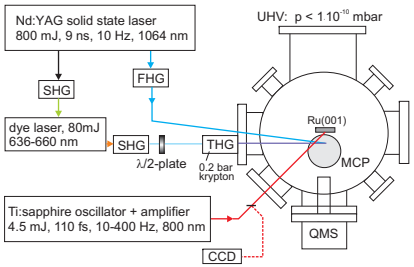
with **REMPI** (**R**esonantly **E**nhanced **M**ulti-**P**hoton **I**onisation)



energy diagram of D_2

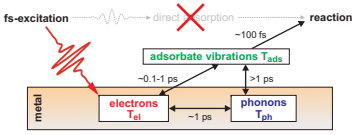


The rovibrational population distribution of the desorbing D_2 molecules is determined with a resonant 2-photon ionization (1+1 REMPI) [3]. By tuning the wavelength of the narrow-bandwidth dye laser the population of the different quantum states can be measured.



SURFACE FEMTOCHEMISTRY: D/Ru(001)

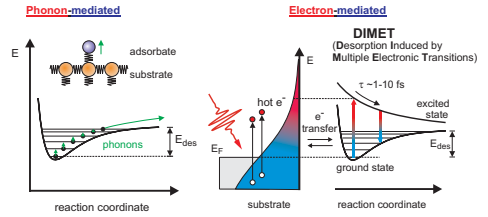
MECHANISMS AND TIMESCALES OF SURFACE FEMTOCHEMISTRY



- "conventional" thermally activated chemistry:
  Substrate electrons and phonons are always in thermal equilibrium. No distinction between electron- and phonon-mediated reaction mechanisms is possible.
- Intense fs-laser pulses create non-equilibrium:
  fs-laser pulses shorter than the electron-phonon coupling time create strong non-equilibrium in the electron and phonon temperatures

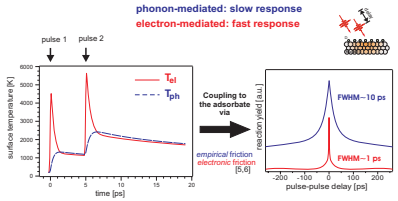
new chemistry?
- by non-**thermal activation**
- **by separation of time scales of energy flow**

SUBSTRATE MEDIATED EXCITATION MECHANISMS IN SURFACE REACTIONS



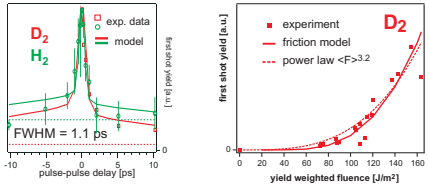
➡ How to distinguish?

DISTINGUISHING ELECTRON AND PHONON MEDIATED PROCESSES



Determination of the FWHM allows to distingiush between electron- and phonon-mediated processes!

PREVIOUS WORK [2] REVEALS THE EXCITATION MECHANISM



narrow 2-pulse correlation

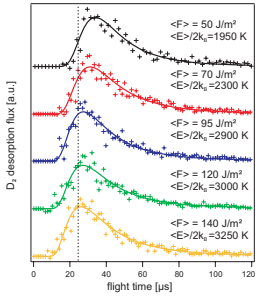
➡ D_2 desorption is electron-mediated!

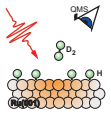
Non-linear fluence-dependenc

➡ **DIMET** (Desorption Induced by Multiple Electronic Transitions)

RESULTS & DISCUSSION

TIME-OF-FLIGHT (TOF) MEASUREMENTS

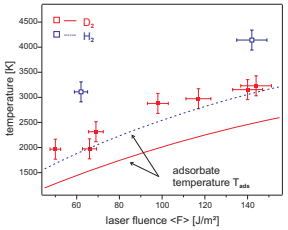




D_2 TOF distributions after fs-laser irradiation of D/Ru(001):

- spectra are well reproduced by a single Maxwell-Boltzmann distribution
- clear shift to shorter flight times, i. e. higher translational energies, with increasing laser fluence

FLUENCE DEPENDENCE & ISOTOPE EFFECT



Fluence dependence

- qualitative agreement between the observed behaviour and the calculated adsorbate temperatures

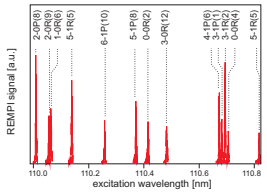
Isotope effect H_2/D_2

- pronounced differences between deuterium and hydrogen

T_{H_2}/T_{D_2}:

<F> [J/m²]	exp.	theo.
60	1.41(22)	1.24
140	1.29(15)	1.30

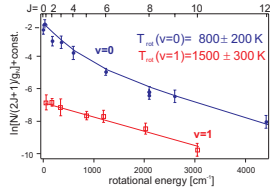
ROTATIONAL AND VIBRATIONAL STATE DISTRIBUTION

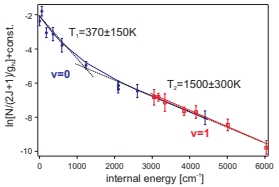


Resonantly enhanced VUV laser ionization spectrum of molecular Deuterium desorbing from D/Ru(001) after femtosecond laser irradiation:

laser fluence: 85 J/m²
pulse duration: 130 fs

D_2 molecules in the states v=0 and v=1 have been detected. (The signal is normalized to the exciting VUV laser radiation)





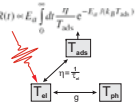
Boltzmann plot of the rotational population distribution:

- The vibrational ground (v=0) state deviates from a single Boltzmann distribution; the first excited state shows Boltzmann-like behaviour.
- An overpopulation for low rotational quantum numbers is observed for v=0.
- Assuming a Boltzmann-like energy distribution for the vibrational degree of freedom, a vibrational temperature of T_{vib}=1200±250 K is deduced.
- The population distribution vs. internal energy is completely described by two Boltzmann-like distributions.
- No increased population of the v=1 state compared to the v=0 state is observed.
- No population of the v=2 state was observed.

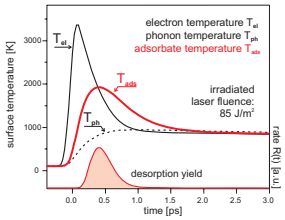
THEORETICAL MODELING

The energy flow in the substrate-adsorbate system after laser excitation can be described by the two-temperature model [4] in conjunction with the electronic friction model [6].
The time dependent reaction rate R(t) allows to calculate a desorption yield weighted adsorbate temperature T_{ads} accounting for the transient process.

$$R(t) = E_a \int_0^\infty d\tau \frac{\eta}{T_{ads}} e^{-E_a/(k_B T_{ads})}$$



E_a=1.35 eV
$\tau_{el}(D_2)$ = 360 fs
$\tau_{el}(H_2)$ = 180 fs



DOES THE MODEL FIT?

Assumption: In the very beginning of the desorption process the energy content in every degree of freedom is the same and given by $k_B T_{ads}$.

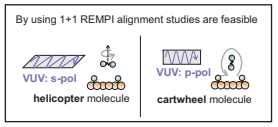
$$\Delta E = E_{tot} - E(T_{ads})$$
$$= 2k_B T_{trans} + k_B T_{rot} + k_B T_{vib} - 4k_B T_{ads}$$
$$= 0$$

translation:	$\langle E_{trans}\rangle/2k_B$=2500±250 K	$\langle E_{trans}\rangle$=220±22 meV
rotation:	$\langle E_{rot}\rangle/k_B$= 910±200 K	$\langle E_{rot}\rangle$= 80±17 meV
vibration:	E_{vib}/k_B=1200±250 K	E_{vib}=100±22 meV
adsorbate temp.:	E_{ads}/k_B=1800±300 K	E_{ads}=155±25 meV

➡ **Excellent agreement between theory and experiment concerning the energy content in the desorbed particle flux**

ALIGNMENT

By using 1+1 REMPI alignment studies are feasible

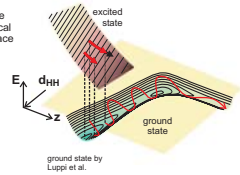


- A positive alignment of $A_0^{(2)}$=0.27±0.10 was found. Molecules desorb preferred as helicopters.
- A possible dependence on laser fluence and quantum state is within the error bars.

CONCLUSIONS

- The observed high temperatures are an evidence for the energy coupling into all degrees of freedom during the fs-laser induced desorption.
- Energy considerations show that the energy content of the particle flux can be described by the calculated adsorbate temperature and is thus in agreement with the electronic friction model.
- First experimental data is available Which provide a basis for theoretical investigations of the ultrafast surface reaction.

Speculations about the involved potential energy surfaces and trajectories have a better fundament now.



ground state by Luppi et al.

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This work was supported by the German Research Foundation (DFG) via:
- SFB 450 "Analysis and Control of Ultrafast Photoinduced Reactions"
- SPP 1093 "Dynamics of Electron Transfer Processes at Interfaces"