

SURFACE FEMTOCHEMISTRY: ULTRAFAST REACTION DYNAMICS DRIVEN BY HOT ELECTRON MEDIATED REACTION PATHWAYS.

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Fundamental insights into the ultrafast dynamics of energy transfer processes at surfaces are of central importance for a microscopic understanding of chemical reactions at solid surfaces, e.g. in heterogeneous catalysis. The detailed investigation of the rates and pathways of energy flow in the adsorbate-substrate system as well as the chemical dynamics has become possible utilizing intense femtosecond laser pulses. Surprisingly, the strong non-equilibrium situation that arises upon irradiation with these pulses results in a new reaction channel caused by hot electron excitation for a number of systems investigated. This electron-mediated reaction mechanism is exemplified here for the model reaction $H_{ad}+H_{ad} \rightarrow H_{2,g}$ on Ru(001) and discussed in the broader context of other simple reactions such as the formation of H_2O , CO_2 and the CO desorption on the same surface.

1 Introduction

In comparison to the gas phase, where femtosecond (fs) laser pulses have been used to probe the ultrashort timescale of bond making and breaking for nearly two decades¹, insights into femtochemistry at solid surfaces have just started to emerge^{2,3}. The extension of femtochemistry methods to the gas-solid interface is complicated considerably by additional experimental challenges: The well-defined preparation and characterization of the initial state of the sample, the low density of reactants of typically one monolayer, as well as the ultrashort lifetimes of excited states due to rapid quenching channels which have to be outpaced by sufficiently large reaction rates, especially on metal surfaces. Furthermore, the chemical mechanisms responsible for surface reactions to occur are entirely different to those in the gas-phase: The presence of a solid-state surface opens a variety of possible excitations and relaxation mechanisms for the adsorbed molecule, which lead to much more complex

excitation mechanisms and pathways of energy flow compared to either gas- or solution-phase chemistry.

This article demonstrates that crucial information about these processes — accessible only on the femtosecond timescale but relevant for "slow", equilibrium chemistry — can be obtained by relatively simple means: The substrate-mediated breaking and formation of chemical bonds between adsorbates by intense fs-laser pulses and probing of the product yields by mass spectrometry.

2 Mechanisms for surface femtochemistry on metals

The key to a microscopic understanding of chemical reactions at surfaces lies in the dynamics of the energy transfer between the substrate and the (reacting) adsorbates. From a simplistic point of view, a metal substrate can be broken down into two subsystems⁴: The ion cores (lattice) and the surrounding electron gas. The energy content of the system can thus be described by two distributions, representing the degree of lattice excitation (collective ion core motions or phonons) and electron gas excitation, both characterized by the temperatures of their respective population distribution functions, T_{ph} for the phonon temperature and T_{el} for the electronic temperature. In thermal equilibrium (or when conventionally heated) $T_{\text{el}} = T_{\text{ph}}$ due to the electron-phonon coupling with a characteristic timescale in the picosecond range (see the illustration of the metal in Fig. 1).

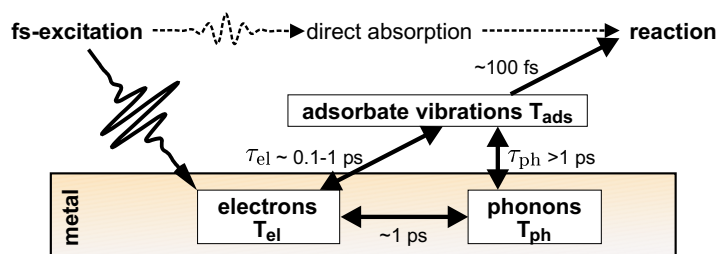


Figure 1. Schematic diagram of the fundamental energy transfer processes and their timescales in the surface chemistry on metals. In fs-photochemistry, the substrate is excited by a fs-laser pulse, which could in principle also lead to a reaction initiated by direct absorption in the adsorbate-substrate complex but is negligible in most cases (see text).

2.1 Excitation mechanisms for adsorbates in surface chemistry

In principle, both of these energy reservoirs may couple energy independently into the adsorbate degrees of freedom relevant for a surface reaction. However, in the traditional picture of a thermal reaction on a metal surface, it is the phonons which drive the system across the activation barrier in the electronic ground state (Fig. 2, right panel). Nevertheless, electrons in the high-energy tail of a thermal Fermi-Dirac distribution can also induce chemical transformations by transient population of normally unoccupied states (Fig. 2, left panel). Such phonon- and electron-mediated processes are fundamentally different, but can not be distinguished by conventional means⁵, where electrons and phonons are always in equilibrium.

The only possibility to gain distinctive information on these processes is to analyze the reactive behaviour on a timescale shorter than the electron-phonon coupling time, where a strong non-equilibrium between substrate electrons and phonons can be achieved by intense fs-laser pulses. These pulses provide a selective excitation by acting only on the electronic subsystem and therefore an ideal tool to gain insight into this so far largely unexplored dynamical behaviour⁶, allowing to establish key reaction mechanisms and parameters such as the pathways and (subpicosecond) timescales of energy flow.

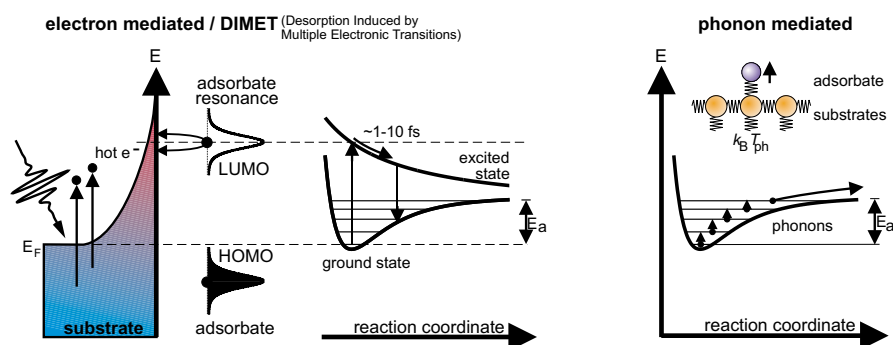


Figure 2. The two principally different substrate mediated excitation mechanisms in surface reactions illustrated for a simple desorption potential well. Left: Electron-mediated energy transfer into a vibrational coordinate of the adsorbate involves (repeated) transfer of electrons from the high-energy tail of a Fermi-Dirac distribution into an unoccupied molecular orbital of the adsorbate-substrate complex (HOMO/LUMO = Highest occupied/lowest unoccupied molecular orbital). This is a non-adiabatic process via an excited state potential energy surface. Right: In contrast, phonon-mediated energy transfer occurs adiabatically, i.e. on the ground state potential surface of the system.

2.2 Ultrafast photochemistry at metal surfaces

Fig. 1 schematically illustrates the fundamental energy transfer processes and their timescales when using an intense fs-laser pulse to photo-induce reactions at metal surfaces. The indirect, substrate-mediated mechanisms are dominant in most cases because of the small optical density of the adsorbate layer (typically a monolayer). Thus, direct absorption in the adlayer is negligible and the energy of the non-reflected part of the fs-laser pulse is absorbed entirely by the metal electrons, creating a hot electron distribution $n(E)$ within the optical penetration depth ($\sim 10\text{--}100 \text{ \AA}$ for $h\nu < 10 \text{ eV}$). This hot electron distribution is initially non-thermal, i.e. the distribution can not be described by Fermi-Dirac statistics. However, very rapid electron-electron scattering leads to a thermalized distribution within several 10 fs for a d-band metal such as ruthenium in the strong excitation regime of laser fluences $> 10 \text{ J/m}^2$.⁴ Therefore on a timescale $> 100 \text{ fs}$ the energy deposited in the electronic subsystem can be described satisfyingly by an quasi-instantaneous electronic temperature T_{el} which characterizes the hot Fermi-Dirac distribution.

These very hot electrons (which may transiently reach thousands of Kelvin above the melting point of the metal⁴) may couple energy into the adsorbate degrees of freedom relevant for a surface reaction via the two completely different mechanisms discussed above in Fig. 2: (i) The hot substrate electrons can directly excite adsorbate vibrations by multiple resonant electron attachment (scattering) into a negative ion resonance. The overall process can be described by an energy transfer time, τ_{el} , typically several hundred fs, characterizing the energy transfer rate from the substrate electrons into the adsorbate nuclear coordinate relevant for reaction. (ii) The adsorbate vibrations can be excited on a somewhat longer timescale of $\tau_{\text{ph}} > 1 \text{ picosecond (ps)}$ via lattice phonons which equilibrate with the hot electrons within a few ps, due to the electron-phonon coupling. This second pathway corresponds to the traditional picture of thermal surface chemistry, in which lattice phonons couple vibrational energy into the reaction coordinate.

How can these fundamentally different mechanisms be distinguished? A direct way to discern the electron- and phonon-mediated adsorbate reaction pathways is provided by a two-pulse correlation (2PC) measurement, which allows for the analysis of the underlying mechanism: Two equally intense pulses are sent onto the adsorbate-covered surface and the time-integrated reaction yield is measured in a mass spectrometer as a function of the pulse-pulse delay. Due to the typical nonlinear dependence of the reaction rate from the incident laser fluence⁷, a correlation function is obtained, whose width critically depends on the excitation pathway. As is illustrated in Fig. 3,

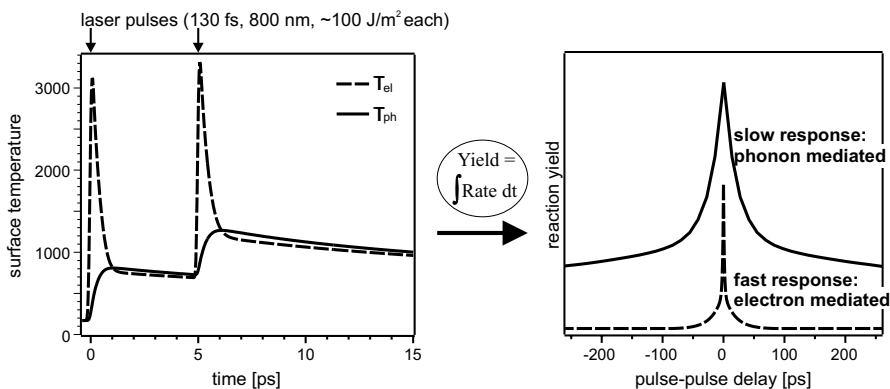


Figure 3. Principle of a two-pulse correlation measurement. Left: Surface temperature transients of Ru(001) calculated with the Two-Temperature-Model⁴ for the excitation fluence used in the H₂ formation experiment (Fig. 4). Right: Schematic illustration of the expected correlation traces which allow to discern the two principal processes – the fast response for an electron-driven reaction and the slow response for a phonon-driven reaction.

a full width at half maximum (FWHM) of the correlation function on the timescale of the e-ph-equilibration time (for ruthenium ~ 1.5 ps) is observed for electron-mediated processes, whereas for phonon-driven processes a much longer timescale on the order of the slow cooling of the phonons into the ruthenium bulk of several 10's to 100's of ps is measured.

A quantitative analysis of such 2PC data can be performed using a friction model^{8,9}, which uses coupling ("friction") coefficients to describe the energy flow from either the electrons⁹, the phonons, or both⁸ into the relevant adsorbate nuclear mode. The energy in the reaction coordinate is then described with a transient adsorbate temperature T_{ads} , from which the reaction rate $R(t)$ can be calculated by use of an Arrhenius expression¹⁰ according to $R(t) \propto \exp(-E_a/k_B T_{\text{ads}}(t))$. The time-integral over $R(t)$ then corresponds to the measured reaction yield in the experiment. Values for the coupling times τ_{el} and τ_{ph} (which are the inverse of the friction coefficients) and the activation energy E_a in the Arrhenius expression are obtained by fitting the results based on the friction model to the experimental 2PC-data.

3 Experimental

Briefly, our commercial laser system delivers 800 nm (1.5 eV), 110 fs pulses with an energy of up to 4.5 mJ per pulse. The Ru(001) sample is mounted in

an ultrahigh vacuum chamber (base pressure $< 1 \times 10^{-10}$ mbar; equipped with a quadrupole mass spectrometer (QMS) and standard surface science tools) and can be temperature-controlled from 30 to 1530 K. A detailed description of the experimental setup together with the surface cleaning, preparation and characterization procedures is given elsewhere.¹¹

The Ru(001) surface can be exposed to oxygen, hydrogen or carbon monoxide via a pinhole doser or a variable leak valve. The adsorbate preparation procedures are the following for the respective investigations: (i) CO₂ formation and CO desorption from the same CO+O co-adsorption structure: 5 L (Langmuir = $1.33 \cdot 10^{-6}$ mbars) of O₂ dosed onto the sample at 600 K (resulting in a 0.5 ML O-coverage with an O-(2x1)-structure), followed by saturation with CO at 95 K.¹² (ii) H₂ formation: H-(1x1)-saturation coverage (1 ML) by dosing 50 L H₂ at 170 K.¹³ (iii) H₂¹⁸O formation: Preparation of an ¹⁸O-(2x2)-precoverage by flashing the exposure of (i) shortly to 1450 K and subsequent saturation with H₂ at 90 K.¹⁴ In all cases thermal desorption spectra of CO or H₂ from the structure were taken and carefully compared to the literature to ascertain the planned structure had been prepared.

In a typical experiment, the Ru(001) surface is covered with the adsorbate structure to be investigated and the reaction yield of the desorbing product species is measured with the mass spectrometer after fs-laser excitation. This is either done by integrating a time-of-flight spectrum or by extrapolation of a depletion curve as shown in Fig. 5 to the first shot yield. Measurements for H₂ are "single-shot" generally, i.e. after each incident laser pulse the adsorbate is again prepared to its initial condition. The laser fluence is generally given as yield-weighted fluence $\langle F \rangle$, where the full spatial profile of the laser pulse as recorded by a CCD camera is taken into account.¹¹

4 Results and Discussion

For the co-adsorption system of O and CO a new reaction channel — the formation of CO₂, which does not occur when the substrate is heated under equilibrium conditions — opens up under fs-laser excitation⁷. In this CO₂-formation channel, energy is transferred directly from the excited substrate electrons into the nuclear degrees of freedom of the oxygen adsorbate. This is in contrast to the "simple" CO-desorption from the same surface, where the conventional picture of heating via the substrate phonons is found to prevail. A friction model analysis gives a typical example for the different coupling times involved: $\tau_{el}=0.5$ ps with an activation energy $E_a = 1.8$ eV for the electron-mediated oxidation, and $\tau_{ph}=1.0$ ps with $E_a = 0.83$ eV for the phonon-mediated CO desorption describe the experimental 2PC data well⁷.

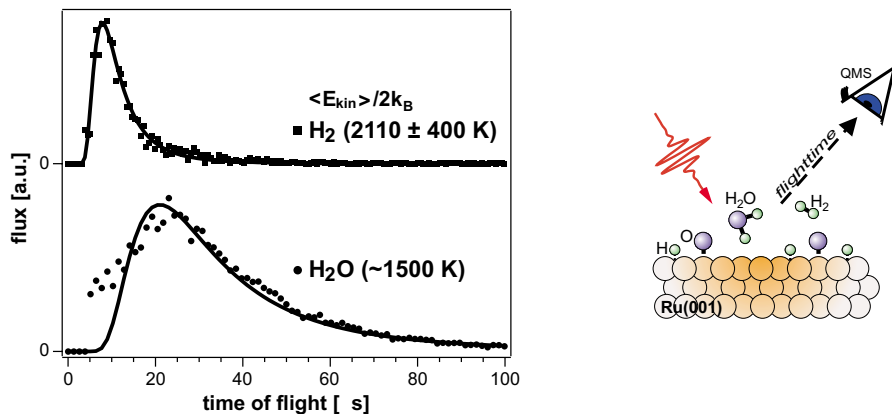


Figure 4. Time-of-flight distributions of the H_2^{18}O and H_2 formation reactions from Ru(001) (incident fluences $\langle F \rangle \sim 110 \text{ J/m}^2$). The spectra are obtained by recording the number of molecules coming off the surface as a function of time after fs-laser excitation; the mean energy given in K (according to $\langle E_{\text{trans}} \rangle / 2k_B$) is calculated directly from the momenta of the measured velocity distributions. The solid line is a modified Maxwell-Boltzmann fit, which deviates considerably for H_2O at short times (future investigations should clarify this; therefore the value of the mean energy for this first dataset has to be treated with caution). The ^{18}O isotope is used to prevent any possible H_2^{16}O background.

In the O+H co-adsorption system, water formation from the Ru(001) surface is observed after fs-laser excitation, a second example of a reaction which is not present with thermal heating. A first result is the time-of-flight (TOF) spectrum shown in Fig. 4. The measured high translational energy of the H_2O molecules (and also of the H_2 molecules) coming off the surface is in accordance with what is expected for an electron-mediated activation mechanism, where a potential barrier has to be overcome for product formation. In analogy to the CO_2 formation we propose for the mechanism of the H_2O -formation, that the O is so strongly bound to the ruthenium substrate that thermal heating is insufficient for a reactive weakening of the Ru-O-bond: Before oxygen activation can occur, the co-reactant (H_2 or CO, respectively) desorbs from the surface. Only by intense fs-laser pulses the Ru-O-bond can be sufficiently activated on an ultrashort timescale, such that a reaction, the formation of H_2O or CO_2 , respectively, takes place. This oxygen activation is sufficiently fast to outpace the competing desorption of the co-reactant.

Fig. 5 shows the two pulse correlation data obtained for the formation of H_2 from a Ru(001) surface saturated with atomic hydrogen (a TOF-spectrum

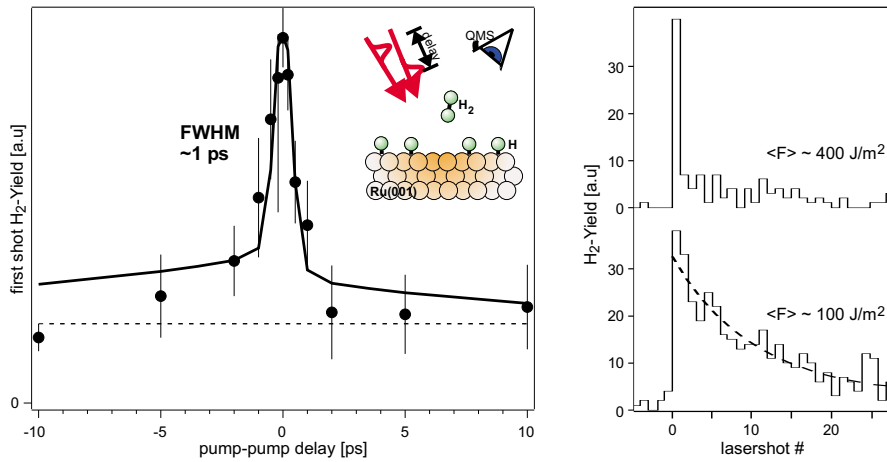


Figure 5. Left: Two-pulse correlation of the H_2 formation reaction yield. The FWHM which is shorter than the e-ph-equilibration time of 1.5 ps indicates that the process is driven by electron-mediated excitation. Right: Decay data of the yield as a function of shot number onto a freshly prepared surface for two different fluences. The 2PC on the left was measured in the low fluence regime, such that saturation of the H_2 formation reaction within one pulse is negligible (the dashed line in the lower panel is an exponential fit for comparison).

is also given in Fig. 4). The FWHM of the two-pulse correlation is on the e-ph-coupling timescale, clearly indicating that the H_2 formation reaction is driven by hot substrate electrons. The 2PC data are well described by the electronic friction model⁹ (solid curve in Fig. 5), which yields a coupling time $\tau_{\text{el}}=160$ fs with an activation energy of $E_a=1.6$ eV. However it is noteworthy, that this reaction can also be initiated via substrate phonons, as is the case when the surface is simply heated thermally. Hence, the H_2 formation can obviously proceed via two different pathways: One involving only the ground state potential energy surface (PES) — the phonon-mediated channel — and a second, completely different, reaction pathway proceeding very efficiently via non-adiabatic coupling to an excited state PES, whereby energy is transferred directly from substrate electrons into the nuclear degrees of freedom relevant for the reaction. It is only with intense fs-laser excitation that the latter channel completely overwhelms the phonon-mediated pathway and leads to very efficient H_2 -formation, such that with high fluences nearly the whole H-layer can be desorbed within one laser shot (Fig. 5, right panel).

5 Summary and Outlook

Summarizing, several elementary reactions of adsorbates from Ru(001) have been investigated induced by fs-laser pulse excitation: Formation of H₂, H₂O and CO₂, as well as the desorption of CO. Some of the most relevant results for these systems are compared in Table 1.

It is found that after intense fs-laser excitation an electron-mediated reaction pathway is opened in all cases except for CO desorption, where the energy transfer into the reaction coordinate is of pure phononic origin. This demonstrates that hot electrons can chemically activate adsorbates — in contrast to the traditional picture of activation solely by phonons. One might argue that the extremely hot electron distributions which give rise to the electron-driven processes are unique to intense fs-laser excitation. Nevertheless, they persist only for the order of ~ 1 ps, whereas the interaction time for thermally heated (much colder) electrons is on the order of seconds. For example, according to Fermi-Dirac statistics, the electron population at 1.7 eV above the Fermi-level¹⁵ for a typical electronic temperature of 6000 K after intense fs-laser excitation is ~ 12 orders of magnitude larger than that of a 600 K thermal distribution. If one defines some effective interaction strength of the hot electron distribution with the ion resonance relevant for the reaction as the typical timescale of the excitation (1 ps vs 1 s) times the typical available number of hot electrons (10^{12} vs 1), the result is quite similar for both cases, indicating that electron-mediated processes might also have to be considered in equilibrium chemistry. However, their relevance will further depend on (i) to which extend multiple electronic excitations of the adsorbate can compete with its vibrational relaxation and (ii) whether there is a competing phonon-driven reaction pathway; both will influence the importance of the respective excitation mechanisms on the "thermal" timescale of seconds and on the ps-timescale very differently. To draw more precise conclusions about the role of electronically non-adiabatic processes in equilibrium chem-

Table 1. Summary of experimental data of all adsorbate systems investigated on Ru(001).

adsorbate on Ru(001)	Product	TOF $\langle E \rangle / 2k_B$	2PC FWHM	Ref.
O-(2x1) + CO	CO	640 K	20 ps	¹¹
	CO ₂	1590 K	3 ps	¹¹
H	H ₂	2110 K	1 ps	this work
O-(2x2) + H	H ₂ O	~ 1500 K		this work

istry, more definite knowledge of the electronic structure of the systems, i.e. exact positions of excited state PES, from theoretical modeling is necessary.

An especially interesting case is the H₂ formation reaction from atomic hydrogen, where a second electron-mediated reaction pathway exists in addition to the well-known thermal channel. Considering the principle of detailed balance, this suggests that in the reverse reaction — the dissociative adsorption of molecular hydrogen on transition metal surfaces — electronic excitations of the adsorbate-substrate system could play an important role in the relaxation processes leading to dissociative adsorption. The experiments presented here show the existence of electronic states which can couple energy in (and out of) the H-Ru(001)-system; their relevance in the dissociative adsorption process of hydrogen has yet to be investigated.

Furthermore, the existence and different timescale of the two energy transfer mechanisms from the excited substrate into the reaction coordinate allows for a rudimentary control of the chemical reactions involved. For example for a chemical reaction where there are two possible products, the outcome of the reaction could be influenced by changing the temporal width of the laser pulses if one of the two reaction pathways proceeds via an electron-mediated mechanism and the other by the slow phonon-mediated process (as e.g. in the CO-oxidation vs CO-desorption case). Depending on the reaction under investigation, this approach should allow to control the outcome of a chemical reaction at least to a certain degree. However, it should be noted that in the case of substrate-mediated excitation coherence is lost by the rapid e-e-scattering events and thus application of optimized laser pulses with a specific shaped phase does not provide a further degree of control. Nevertheless, if a direct excitation pathway is accessible in the system, as has been recently demonstrated for Cs/Cu(111)¹⁶, this might open the perspective for optimum control scenarios of surface reactions.

Acknowledgments

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