

# Ultrafast dynamics of recombinative desorption of hydrogen from a Ru(001) surface

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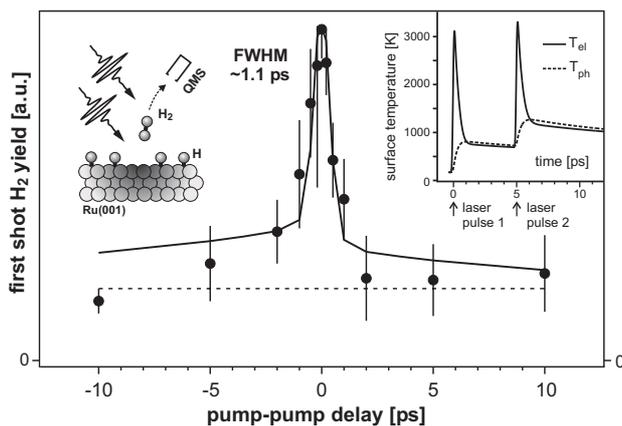
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**Abstract.** Femtosecond-laser excitation induces recombinative desorption of molecular H<sub>2</sub> from atomic hydrogen on a ruthenium surface. The measured ultrafast timescale of this surface reaction reveals an excitation process mediated by hot substrate electrons. A coverage dependent isotope effect indicates a collective reaction mechanism whereby vibrationally excited H atoms modify the reactivity of coadsorbed species.

**Introduction.** The dynamics of energy transfer processes at surfaces are of fundamental importance for a microscopic understanding of chemical reaction at solid surfaces, e.g. in heterogeneous catalysis. In conventional chemistry with phonons and electrons always in thermal equilibrium, no detailed information can be obtained on the pathway of the energy flow between the substrate and the adsorbate. However, when a metal substrate is excited by an intense femtosecond-laser pulse, a transient non-equilibrium between the electronic and phononic temperatures is created, which lasts on the order of the electron-phonon coupling time (for ruthenium  $\sim 1$  ps) and allows to distinguish electron-mediated from phonon-mediated surface reactions [1].

**Experiment.** The appropriate experimental approach is to measure the two-pulse correlation (2PC) of the respective reaction yield. To this end, the fundamental output of an amplified Ti:sapphire femtosecond-laser system is split in two equally intense portions and both beams are sent time-delayed onto the sample mounted in an ultrahigh vacuum chamber. The yield of the desorbed products is detected with a quadrupole mass spectrometer as a function of the pulse-pulse delay.

**Results and discussion.** Figure 1 shows such a 2PC of the desorption yield for the formation of molecular H<sub>2</sub> from atomic hydrogen on an H-saturated Ru(001) surface. The narrow full width at half maximum (FWHM) of  $\sim 1.1$  ps unambiguously indicates that hot substrate electrons are the driving force behind this recombinative desorption [1,2]. The experimental data are well reproduced by a simulation (solid line) using the two-temperature model (electronic and phononic temperatures  $T_{el}$  and  $T_{ph}$ ) [3]. Friction between the substrate and the adsorbate [4,5] couples energy from the substrate subsystems to the adsorbate vibrations and hence into the relevant reaction coordinate. The electronic friction model [5] used here to describe the 2PC data for hydrogen yields an ultrafast coupling time for the H<sub>2</sub> formation of only a few hundred femtoseconds.



**Fig. 1.** Two-pulse correlation of the H<sub>2</sub> desorption yield showing a narrow FWHM of ~1.1 ps. The inset displays typical time profiles for the electronic and phononic temperature at an exemplary pulse-pulse delay of 5 ps.

In addition, a pronounced isotope effect in the reaction yield  $Y(\text{H}_2):Y(\text{D}_2)$  of 10:1 taken from isotopically pure saturation coverages corroborates the electronic origin of the desorption process.

Molecular hydrogen can also be formed “thermally” in this system, i.e. by conventionally heating the surface. Comparing desorption measurements occurring via either the thermally or the hot-electron driven pathway exhibit the uniqueness of the “femtochemical” reaction with clear evidence for a novel mechanism: The latter process involves a concerted action of more partners than only both reactants forming the respective hydrogen molecule. Experimentally, this is seen in significant changes of the isotope yield ratio of the desorbed molecular hydrogen if the mixture of the coadsorbed atomic H and D on the surface is varied.

For exemplary H:D mixtures, Table 1 summarizes the relative desorption yields of the three isotopic species obtained under thermal equilibrium and laser excitation conditions, respectively. Thermal desorption experiments (TD) with the mixed isotope HD result in the statistically expected relative isotope ratio H<sub>2</sub>:HD:D<sub>2</sub> of 1:2:1. Additional data from mixtures ranging from ~15:85 up to ~85:15 H:D (prepared by precovering the clean surface with HD and subsequently saturating the surface with the respective pure isotope) further corroborate that second order rate equations hold in the case of “thermal” surface chemistry. According to chemical kinetics, the rate of a bimolecular reaction of the form  $A + B \rightarrow AB$  scales with the concentrations of each of the reactants [A] and [B]. In contrast, clear deviations are found in the femtochemical case. As seen in the center column of Table 1 (*italic numbers*) and different from the TDS data, more D<sub>2</sub> with respect to H<sub>2</sub> (i.e. 1:3) is formed than one would expect supposing the isotope ratio of 1:10 (**bold numbers**) is independent of the reactants’ concentration and is solely due to the mass difference.

**Table 1.** Relative yields of H<sub>2</sub>, HD, and D<sub>2</sub> from Ru(001) by thermal heating under equilibrium conditions *versus* fs-laser excitation for differently mixed coverages.

Yield	H : D ratio of the coverage in percent					
	100:0		50:50		0:100	
	thermal	fs laser	thermal	fs laser	thermal	fs laser
H <sub>2</sub>	1	<b>10</b>	1	3	-	-
HD	-	-	2	4	-	-
D <sub>2</sub>	-	-	1	1	1	<b>1</b>

Summarizing, with femtosecond-laser excitation a higher H concentration [H] seems to enhance both the formation of H<sub>2</sub> and D<sub>2</sub> and thus second order chemical kinetics fail to describe this femtosecond-laser driven reaction.

Instead, we propose the following collective reaction mechanism: The lighter hydrogen H acts an antenna, when the surface is laser-excited with a femtosecond pulse. Due the electronic nature of the energy flow from the substrate to the adsorbate layer, atomic H in mixed layers is excited first, since its coupling time is by a factor of 2 shorter than that of atomic D. A subsequent change of the interaction between neighboring atoms, e.g. repulsion between the excited H and a “cold” D or changes in the potential energy landscape for the respective reaction partners, would then promote the recombination of the deuterated species. Theoretical calculations are still underway to more quantitatively describe the observed phenomena and might prove that our results have more general implications on surface chemistry.

**Acknowledgements.** Financial support by the Deutsche Forschungsgemeinschaft through Sfb 450 is gratefully acknowledged.

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