

## **Femtochemistry, vibrational and electronic relaxation dynamics in ultrafast processes at surfaces**

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Chemical reactions involving species absorbed on a metal surface are mediated through excitation of electrons and/or phonons of the substrate. If such a surface reaction is initiated by absorption of an ultrashort laser pulse, distinct differences to a thermally driven reaction can be observed. However, time-resolved experiments provide detailed insights into the underlying reaction mechanism, the flow and dissipation of excitation energy and the respective timescales, which are otherwise not accessible.

In a first example, the femtosecond-laser induced  $\text{H}+\text{H} \rightarrow \text{H}_2$  recombination reaction on a Ru(001) surface will be presented. A purely hot-substrate electron-driven desorption mechanism based on nonadiabatic coupling between electronic and nuclear degrees of freedom is found. This is manifested in a narrow two-pulse correlation and a huge isotope effect in the reaction yield. State-selective detection of the desorbing molecules, in addition, provides information on the energy partitioning during the reaction. Finally, significant adsorbate-adsorbate interactions crucially determine the outcome of the hydrogen recombination. These effects are believed to be also of relevance in conventional, i.e. thermal, surface chemistry.

Vibrational spectroscopy based on sum-frequency generation represents an ideal tool towards time-resolving a surface reaction en route from the educt to the product state. How this experimental techniques also contributes to structural information of an adsorbate layer will be shown in the case of water ( $\text{D}_2\text{O}$ ) on Ru(001). In addition, the vibrational relaxation dynamics in thin  $\text{D}_2\text{O}$  ice layers are investigated by means of the free induction decay.

Finally, time-resolved THz spectroscopy (TRTS) probes the dynamics of low-energy excitations in the few meV range. Since external adsorbate modes like the soft adsorbate-substrate stretch or librational motion are directly connected to the reaction coordinate, TRTS is an appealing approach to study surface reactions. First successful applications of this technique to the charge carrier dynamics such as electronic energy and current relaxation in thin graphite sheets and carbon nanotubes will be presented.