ABSTRACT

Using ultrafast extreme-ultraviolet pulses for time-resolved dynamics of molecules chemisorbed on metal surfaces

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The time-resolved observation of chemical reactions on metal surfaces represents a very important step towards understanding how these surfaces work as catalysts. Developming techniques that would allow us to observe these dynamics is therefore very important for both scientific and industrial applications. However, experimental methods that combine both surface sensistivity and sub-picosecond time resolution have proven to be challenging. In this thesis, I describe a ”Time-Resolved extreme-Ultraviolet Photoemission Spectroscope” (TR-UPS), that allows us to observe the dynamics of adsorbate molecules on surfaces with femtosecond time resolution. This experimental tool combines state-of-the-art techniques for generating EUV light (42 eV photon energy, sub-10 fs pulse width) using high-harmonic generation of intense ultrafast infrared pulses, with the technique of photoelectron spectroscopy.

Two experimental investigations have been performed with the TR-UPS. A saturation layer of O_2 adsorbed onto a Pt(111) single crystal surface at 77 K results in the oxygen preferentially residing on the bridge-site of the platinum surface. By exciting the O_2/Pt system with an ultrafast pulse, we can then observe time-dependent changes in the electronic structure of the surface/adsorbate that corresponds to movement of the oxyen from the bridge-sites to the hollow-sites of the platinum surface. This change occurs in about half a picosecond. Subsequently, the oxygen molecules relax back to their original configurations in under 5 ps. In the second experiment, CO molecules are introduced onto the Pt(111) surface. The CO molecules are known to adsorb onto the platinum surface in an upright position, parallel to the platinum surface normal. Using symmetry properties of the CO molecular orbitals, I determine the oscillation period of the frustrated translational mode of the CO molecules to be about 950 fs.