

# Contrasted behaviour of terrace and edge CO adsorbed on Pd nanoparticles studied by pump probe SFG

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Nanoparticles are the subject of many studies due to their applications in various fields, like plasmon enhanced optical detection of biological molecules, or nanocatalysis. Using linear absorption femtosecond laser techniques, the sensitivity has reached single nanoparticle detection even in biological environments. The dynamics of nanoparticles following femtosecond laser excitation has been studied by linear absorption pump-probe experiments. It was shown the increasing importance of surface scattering of the electrons as the particle size decreases, and the ability to excite vibrational modes of the nanoparticle.

To obtain more specific information on processes occurring at the nanoparticle surface following a femtosecond laser pulse, a technique able to detect specifically adsorbed molecules is required. Pump probe sum-frequency generation (SFG) with femtosecond pulses is a unique tool to monitor photodesorption [1], surface diffusion [2], and energy relaxation on single crystals [1,3]. In this work, we report such experiments on CO adsorbed on a model catalyst, namely Pd nanoparticles epitaxially grown on a MgO film grown on Ag(111), of size a few nm. SFG spectra show CO at terrace bridge adsorption site and at several sites located at nanoparticle edges, in agreement with a previous SFG study done with picosecond lasers [4]. Vibrational frequencies are observed to vary with coverage and particle size. Pump probe experiments show broadening and red shift of vibrational bands similar to the case of single crystals, and photodesorption is observed. The most striking feature is that terrace sites are much more sensitive to electronic excitation and photodesorption than edge sites, showing that photoelectrons are weakly coupled to CO at edge sites.

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