

## Ultrafast Laser Excitation of CO/Pd (111) Probed by Sum Frequency Generation (SFG): Pump Laser Energy Effect on the Induced CO Photo-desorption

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### Abstract:

The desorption of CO from Pd (111) induced by femtosecond laser pulses is probed by IR + vis sum frequency generation (SFG). A large redshift of the main band, a broadening, and a strong decrease in intensity are observed; these originate from coupling of C-O stretch to low frequency modes (the frustrated rotation). Simulation based on two temperature models of electron and phonon heat baths within the substrate, show that CO desorption from the Pd (111) is an electron-mediated process, and this corresponds well with the results obtained by two pulse correlation. SFG spectra show a development of a second band at high frequency at negative delay, which disappears at positive delay, due to an interference phenomenon between disturbed and undisturbed states of the SFG pulse. The CO desorption is becoming important with increasing the pump energy. We compared CO photodesorption from Pd (111) to others metals, indeed the most probable hypothesis that makes the difference between metals is the position of CO  $2p^*$  adsorbate resonance, into which substrate electrons may be excited. Other factors may play a role as the distance and the strength of CO-Metal.

The infrared-visible sum-frequency generation (SFG) spectroscopy response of a composite interface comprising molecules, spherical nanoparticles, and a substrate is modeled in the dipolar approximation. The spheres modify the local electric fields felt by the molecules grafted on either the surfaces of the particles or the substrate below the spheres. In the case of plasmonic spheres, the excitation of their surface plasmons results in amplifications of the molecular SFG signals at the incoming visible and SFG frequencies for both types of molecules. The spectral evolutions of these amplifications are described as a function of the natures of the metal, the molecules, and the substrate; the chemical groups involved; and the surface density of such nanoparticles on such substrate and their surface coverage. The latter parameter is shown to be the most source of SFG from molecules adsorbed on these highly centrosymmetric objects. Models are compared to experimental data, and excellent agreement is found for the amplification of the SFG vibrational signature of a grafting monolayer sandwiched between a silicon substrate and gold nanospheres.

Understanding adsorbate dynamics on surfaces is crucial to many phenomena, ranging from heterogeneous catalysis to sensing devices. Over the past 30 years, time-resolved vibrational and electronic spectroscopies, based on femtosecond laser pulses, have made many important contributions to our understanding, with the investigation of vibrational excitation, diffusion, desorption, and reaction. Due to the high absorption in the cross-section of metal surfaces, compared to most adsorbates, the photon energy is first deposited in the metal electrons

followed by energy transfer to phonons and the adsorbate. The interpretation of spectra, therefore, generally rests on the very fact that hot electrons exist for around 1ps from the before equilibration with phonons. Thus, any sub-picosecond response is thought to identify the signature of non-diabatic dynamics, in which energy will be directly shifted between hot electrons and therefore the adsorbate vibrational modes.

Due to the massive energy difference between the typically observed internal stretching (IS) mode of CO or NO and the energy scale of hot electrons, the generally accepted model involves direct energy transfer between hot electrons and low energy vibrational modes, which, in turn, couple anharmonically to the observed high energy mode. The majority of studies have focused on the vibrational dynamics of CO, which, so far, are generally attributed to coupling between hot electrons and therefore the frustrated rotation (FR) mode; for instance, on Ru (001) and Pt (111). The origin of the observed redshift of the C-O stretch, while all the surface electrons are hot, is assumed to be caused by excitation in the frustrated translational (FT) mode, which is indirectly heated through.

Here, we confirm for our further understanding of nonadiabatic coupling between electrons and vibrations and modify the vibrational dynamics by decoupling CO from the bulk metal through coordination to a metalloporphyrin on a metal substrate. The fact in these systems stems from the profound influence in which small ligands might wear the adsorbed metalloporphyrin's electronic and magnetic properties. For metalloporphyrins adsorbed on metal substrates, coordination of the NO decouples the metal ions from the metal substrates, partly reversing changes within the electronic structure caused by interaction with the underlying metal and, additionally, changes the spin state of the metal ions. A recent inelastic tunneling study of CO, coordinated to RuTPP adsorbed on Cu (110), revealed that CO desorption by injection of holes from a scanning tunneling microscope tip proceeds in an unusual two-carrier process, which might be associated with CO decoupling the Ru ion from the copper surface. Existing time-resolved studies have only been administered on CO ligands at heme proteins. Upon absorption of photons by the heme, CO is photodissociation and transfers to a close-by docking site. Ultrafast visible pump mid-IR probe measurements showed that CO rotated upon dissociation and moved to the new site in but a picosecond.

Here now, we investigate all the nonadiabatic vibrational dynamics of CO from CO-RuTPP/Cu (110) under photodesorption conditions. The frequency of such C-O stretch mode of CO-RuTPP shows a blue shift during coupling of the hot electrons under photodesorption conditions. This phenomenon is more easily explained if the nonadiabatic dynamics of CO/Cu (110) aren't caused by anharmonic coupling of the interior stretch to low frequency vibrations, but instead by charge transfer to the CO  $2\pi^*$  state.

The Electron-vibration coupling of CO on the RuTPP-covered Cu (110) surface was investigated by pump-probe SFG under photodesorption conditions. Femtosecond visible pump-sum frequency probe spectroscopy revealed that coupling with hot electrons was significantly altered by introducing the RuTPP monolayer, because the frequency redshift, typical for the interior stretch of CO adsorbed on the metal surfaces, that disappears and is displaced by a blue shift at short delay times. Interpretation within the framework of intermode coupling in

between IS, FR, and FT is problematic. Rather, we propose that the upshift of the CO  $2\pi^*$  state on RuTPP suppresses the frequency redshift caused by charge transfer from hot electrons and reveals the blue shift caused by electron-mediated coupling between the coherently excited internal stretch and every one other low frequency modes within the system, as recently proposed in the electron-mediated phonon-phonon coupling mechanism.