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THEORETICAL STUDY OF EXCITED ELECTRONIC STATES AT SURFACES, LINK WITH PHOTO-EMISSION AND PHOTO-DESORPTION EXPERIMENTS

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Abstract. Excited electronic states at surfaces are very often invoked as intermediates in reaction mechanism at solid surfaces. Indeed, formation of an excited state brings energy into the system and, most importantly, opens the way toward rearrangement processes: the potential energy surfaces describing the heavy particle motion are different for the ground and excited electronic states, so that electronic excitation triggers a motion of the atoms at the surface. In that context, the lifetime of the excited state as well as its coherence time are key parameters for the reaction mechanisms: they determine the extent to which a given excited state can induce a reaction or possibly lead to its quantum control. Various experimental techniques yielded many detailed results on the excited electronic states and their dynamical properties (energy, lifetime and coherence time): time-resolved 2-photon photo-emission (TR-2PPE) in the fs-domain and scanning tunnelling spectroscopy (STS) with atomic resolution.

The talk will review a series of results on excited electronic states at noble metal surface systems(Gauyacq et al, 2007). Based on theoretical results, it will show how the presence of a projected band gap on certain noble metal surfaces qualitatively influence the dynamics of the excited electronic states and in particular how it partly blocks the electron transfer between an adsorbate and the surface, allowing the existence of long-lived electronic states localized on the adsorbates. In the alkali/noble metal systems, the formation of the long-lived state corresponds to the transient capture of an electron by the adsorbate and the change of charge state of the adsorbate induces an outward motion of the adsorbate from the surface. Recent results on these photo-induced adsorbate vibration and desorption processes will be presented.

References

Gauyacq, J. P., Borisov, A. G. and Bauer, M.: 2007, *Prog. Surf. Sci.*, **82**, 244.