

# Vibrational recognition of CO adsorption sites on transition metal surfaces

Ismaila Dabo,<sup>1</sup> Andrzej Wieckowski,<sup>2</sup> and Nicola Marzari<sup>1</sup>

<sup>1</sup>*Department of Materials Science and Engineering, Massachusetts Institute of Technology*

*Cambridge, MA, USA*

<sup>2</sup>*Department of Chemistry, University of Illinois at Urbana-Champaign  
Urbana, IL, USA*

We have studied the vibrational properties of carbon monoxide adsorbed on platinum using density-functional perturbation theory in the GGA-PBE approximation. The calculated frequencies for the localized CO stretching mode are found to be in excellent agreement with spectroscopic measurements. The relative shifts that take place when the surface is covered by ruthenium islands or monolayers are also correctly predicted. This agreement for both shifts and absolute vibrational frequencies is made more remarkable by the generally-poor performance of local and semilocal exchange-correlation functionals, that fail even in predicting the most stable adsorption site for CO on metal surfaces. A detailed analysis of the chemical origin for the frequency shifts of the CO stretching mode as a function of the adsorption site has been carried out. In particular, we present a novel orbital-resolved force analysis and a GGA + molecular U approach that allow us to investigate the effects the orbital hybridizations on the CO vibrational frequencies, and to rationalize the DFT accuracy in predicting correct vibrational spectra while failing in predicting the correct energetic sequence.