

Title: **Probing CO Adsorption on fcc Metals**

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1. SUMMARY

The computational study on CO adsorption on coinage (Cu, Ni, Ag, Au) and Pt group (Pt, Pd, Ir, Rh) metal surfaces is interesting due to their application in catalysis where CO can be a reagent intermediate, product, as well as a poison, or used as probe molecule to characterize the metal surfaces transformation reactions. All these metals show a cube-shaped crystalline structure centered on the faces (fcc) where the most stable surfaces belong to the lowest Miller index — (100), (110), (111). We studied the CO stability on the different metal surfaces, so as to determine which position and conformation is the most stable, including upright and flat conformations, and different surface sites, with the aim of analysing the bond.

The study, carried out using Density Functional Theory (DFT) on slab models for the surfaces, and using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional reveals the strong position to adsorb CO, C-connected, in an upright position, although different sites can be occupied. The stronger the bond, the closer the CO to the surface, and the longer the CO bond elongates. Apparently, the adsorption is influenced by the surface coordination number and surface energy. Accordingly, the surface bond measures the CO bond, reducing its $\nu(\text{CO})$ stretching frequency whose values are quite connected to the surface connectivity, being Top>Bridge>Hollow. The different occupancy may help distinguishing different types of CO, over surfaces. The strong nobility of Ag and Au, and the poisoning by CO of Pt group metals is also understood based on the computed adsorption energies.

Keywords: CO, Transition Metals, Density Functional Theory, Adsorption Energies, Catalysis, IR, Spectroscopy.