SERS and DFT study of indigo adsorbed on silver nanostructured surface

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Surface-enhanced Raman spectroscopy has emerged as a widely used tool in the identification of organic dyes in works of art. Indigo is among the most used organic pigment, its identification can therefore give important information about the provenience and the making of the investigated work of art. In this work, we combine Surface Enhanced Raman Spectroscopy (SERS) experiments with density functional theory (DFT) computations of the Raman frequencies of indigo and an indigo molecule adsorbed onto a silver surface made of 16 silver atoms. The SERS spectrum of a molecule adsorbed on a metallic surface, in fact, can differ from the corresponding Raman one. The knowledge and the comprehension of the SERS spectrum then are mandatory in dyes identification. Experimental SERS spectra were acquired using ad hoc SERS active substrates consisting of pulsed laser ablated silver nanoparticles deposited onto a polishing sheet. The polishing sheet surface roughness is able to remove some pigments grains from the surface of a work of art without damage. DFT calculations provide a good description of the observed SERS spectra, in particular, the indigo-Ag_{16} structure gives a better description with respect to structures where only one or two silver atoms attached to the indigo molecule are considered.

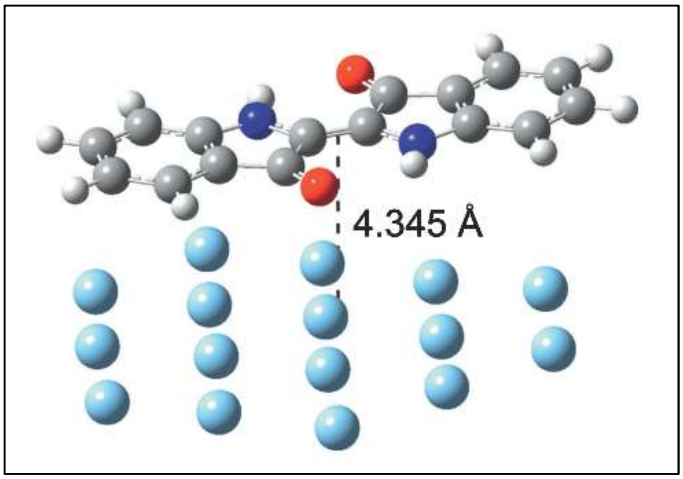

Fig.1: Indigo-Ag 16 complex optimized structure; colour code: red = oxygen, blue =nitrogen, gray = carbon, white = hydrogen, cyan = silver. The molecule lies parallel to the Ag surface at a distance of 4.345 Å. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)