

The analysis of dyes in cultural heritage samples is a well-known challenging task, due to their inherent high tinting strength and consequent low concentration in the carrying matrix. This fact severely limits the number of analytical techniques that can be efficiently and micro-destructively employed for their detection and unambiguous identification. Raman spectroscopy has been employed with consistent difficulties associated to the sample typology itself and the amount necessary to obtain good quality spectra. The introduction of Surface-Enhanced Raman Spectroscopy (SERS) to the field of conservation science has made the study of such materials possible and more straightforward, both as free molecules and as in artworks. This is possible thanks to SERS ability to yield good signal-to-noise ratio spectra from a very low amount of sample, as well as to the quenching of the fluorescence emission, an additional obstacle when working

with traditional Raman spectroscopy. Density Functional Theory (DFT) is a quantum-mechanical atomistic simulation method to compute a wide variety of properties of almost any kind of atomic system, such as molecules crystals, surfaces, etc. DFT belongs to the ab initio family as they can predict material properties for unknown systems without any experimental input. Vibrational frequencies are among these properties that can be simulated by DFT. Thus, Raman spectra can be calculated together with the associated normal modes, i.e. stretching and bending vibrations. By comparing the experimental and the calculated Raman spectra, the vibrational normal modes can be assigned to the experimental bands. The adsorption geometry of the dyes on the SERS substrate can be elucidated taking into account the SERS selection rules.