

SERS substrates for pigments detection in works of art: a combined DFT and experimental study

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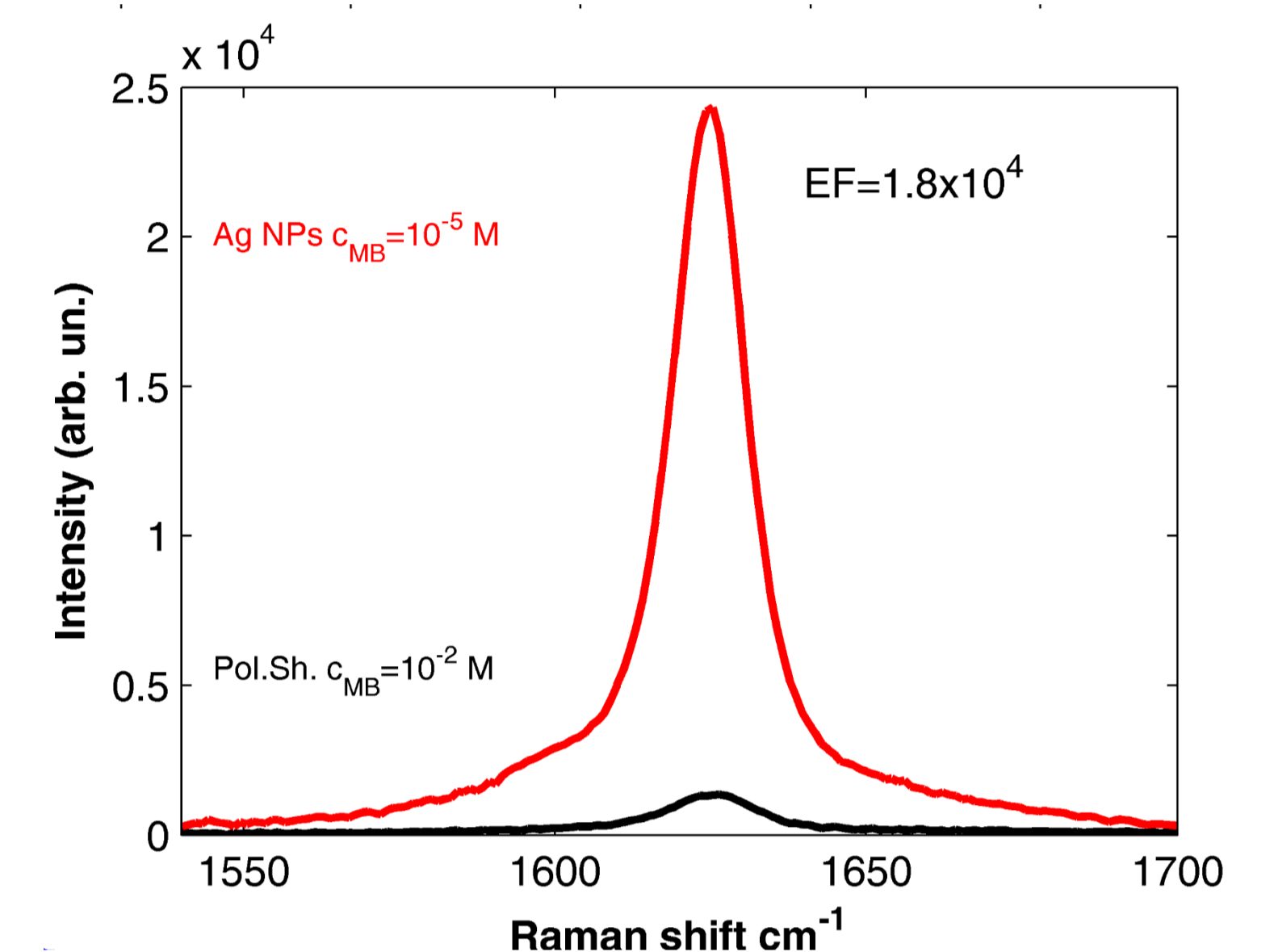
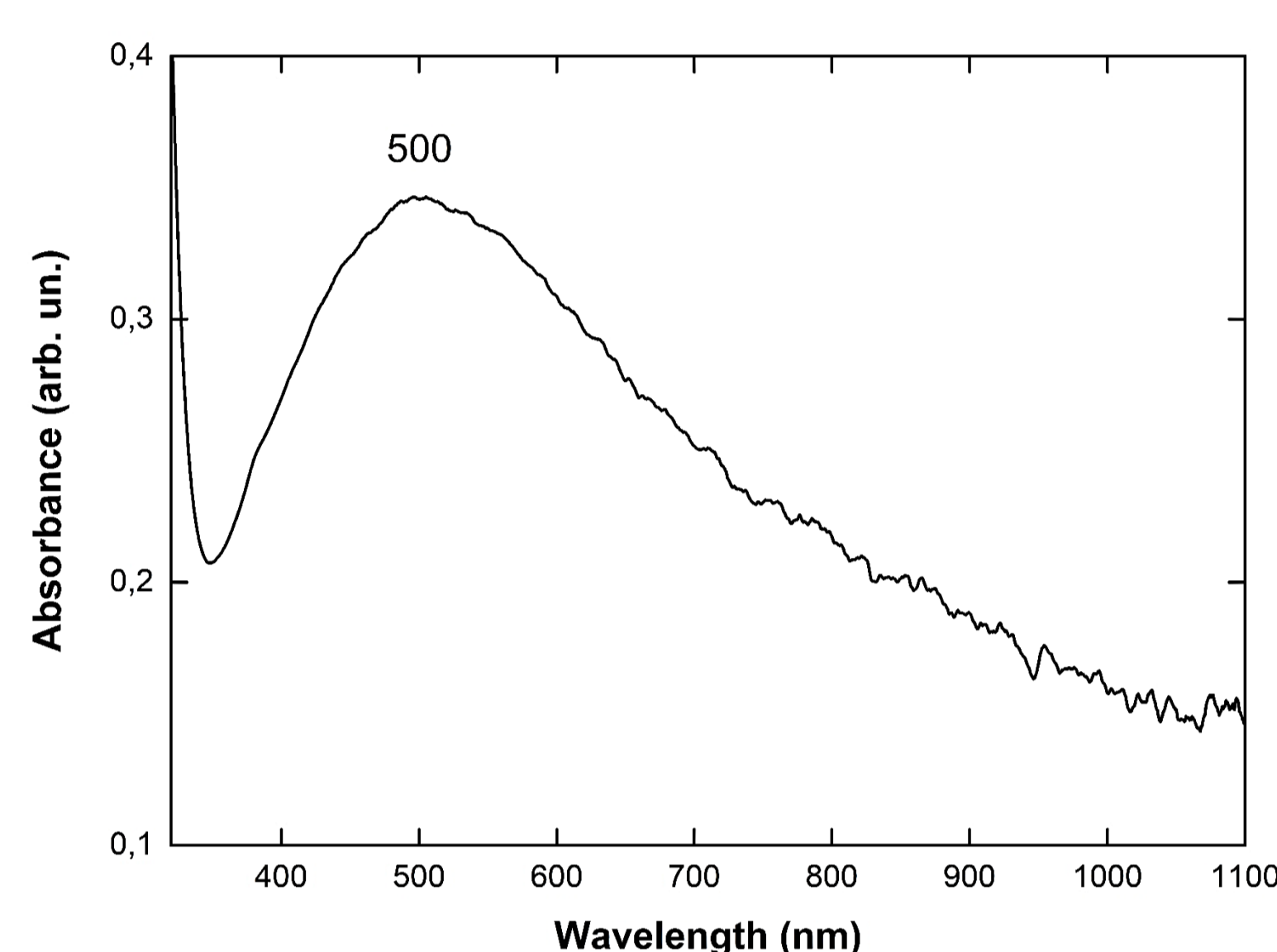
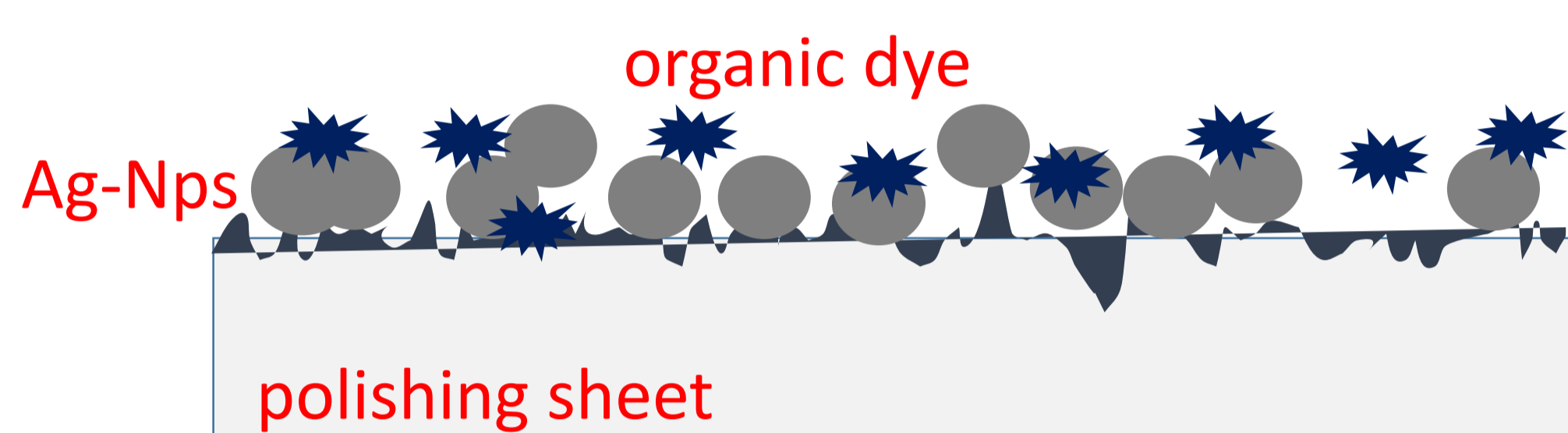
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Abstract

Surface-enhanced Raman scattering (SERS) spectroscopy represent a valid approach in the identification of organic dyes in works of art. [1] In this work we present SERS substrates, made by a thin layer of silver and gold nanoparticles, deposited on sandpaper sheets by means of pulsed laser ablation technique (PLA). [2] SERS substrates are designed and realized specifically to detect pigments in the field of Cultural Heritage. [3] The so obtained substrates can be gently swabbed, for example, on a painted surface or on small decorated fragments in order to collect small quantities of the superficial layer. Then Raman spectra are acquired on the substrate surfaces avoiding in such a way direct laser exposition of the work of art. Moreover, DFT (density functional theory) calculations were carried out in combination with SERS experiment to understand the nature of interactions between pigment and nanoparticles for indigo [4] and methylene blue.

SERS-Substrates

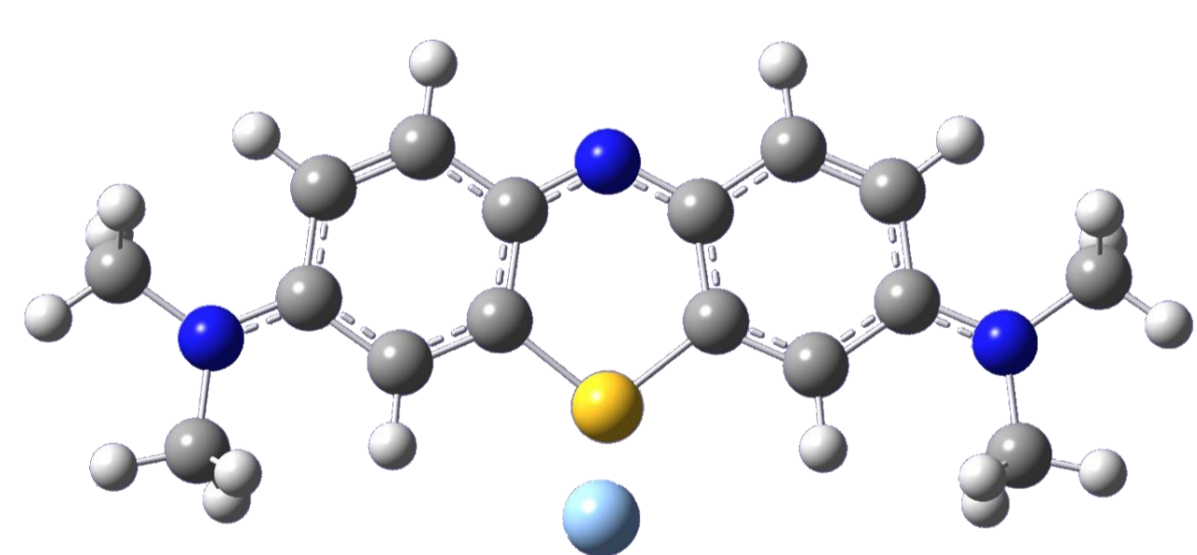


The substrate used for the SERS experiment was a polishing sheet with a surface roughness of about 50 nm. The polishing sheet was coated by silver nanoparticles deposited by means of pulsed laser deposition technique (PLD). We estimated the SERS enhancement factor (EF) of the NPs decorated polishing sheets using an aqueous solution of methylene blue (MB). A 10^{-2} M MB solution was used in order to observe a clear Raman signal from the uncovered polishing sheet, while a 10^{-5} M solution was used on the Ag decorated polishing sheet. By comparison, of the peaks intensities and taking into account the difference in the MB concentrations, the estimated SERS enhancement factor resulted of 1.8×10^4 , showing that a good SERS activity was preserved on the polishing sheet.

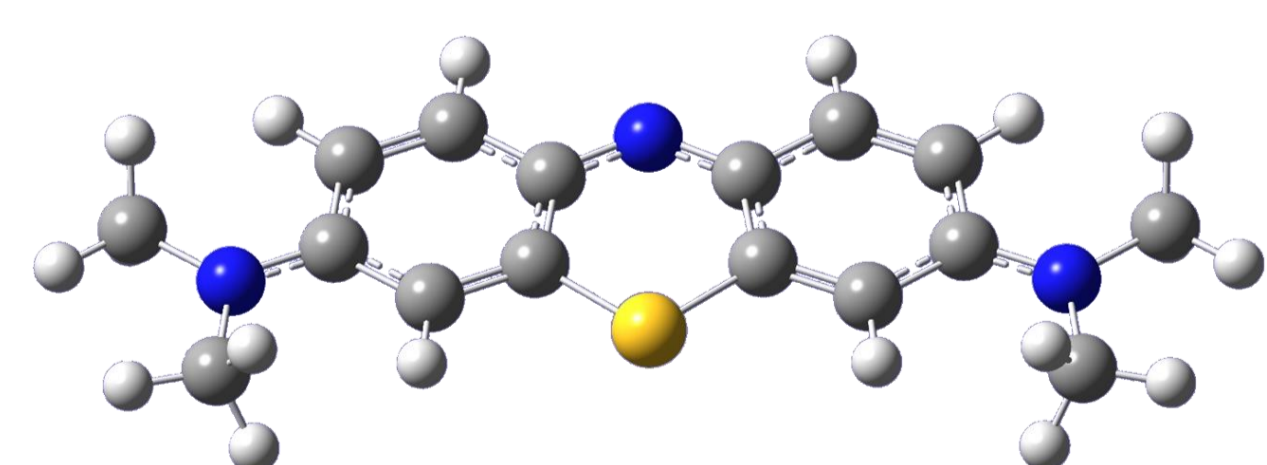
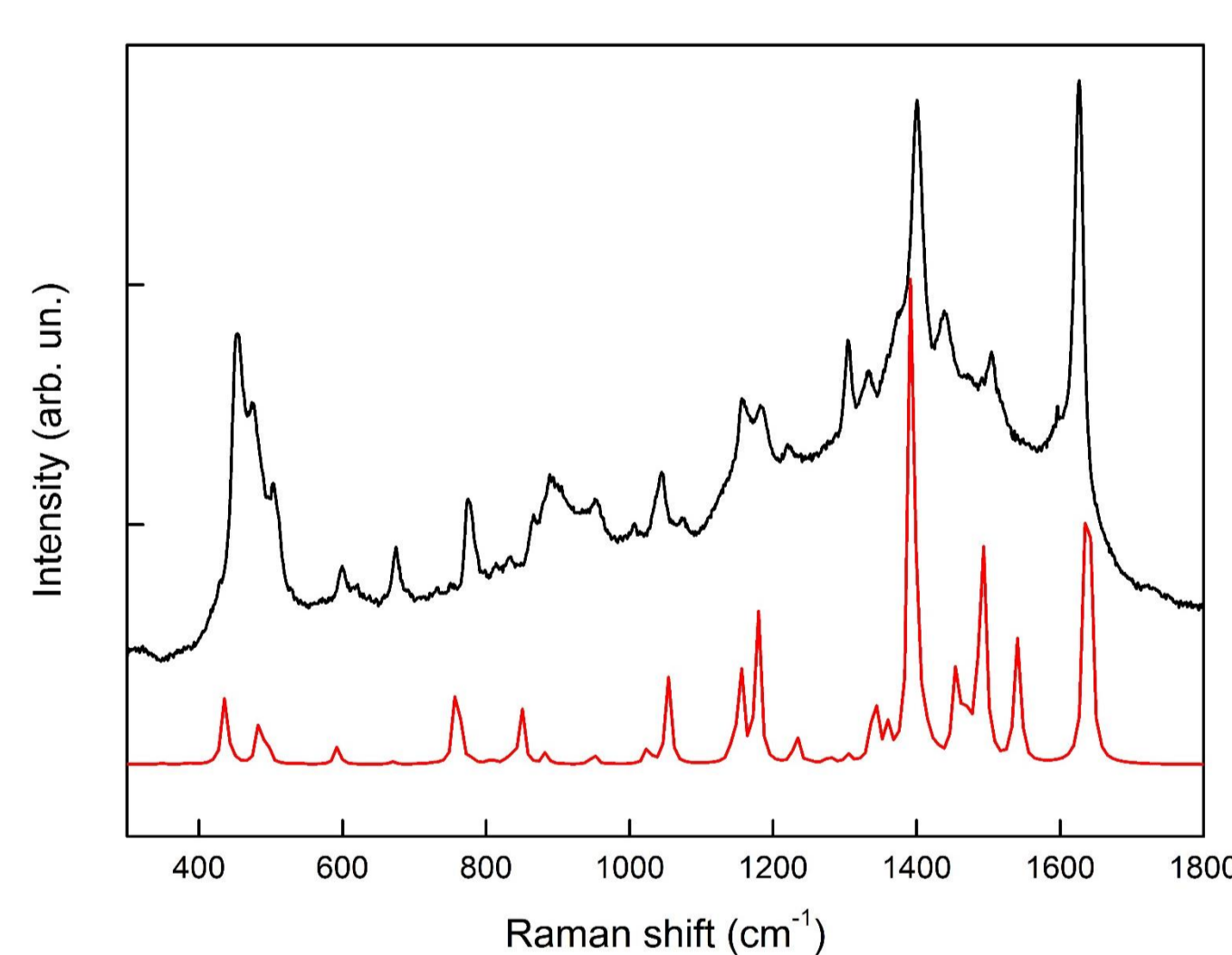
DFT-calculation

We modeled the Ag-dyes structures to evaluate their energetic stability together with their Raman and SERS theoretical spectra, in order to be compared with the outcomes of the experimental results. The isolated dyes (MB and indigo) were previously optimized at B3LYP/6-31+g(d,p) level of theory. A second structural optimization was performed on the dye-Ag system, followed by Raman spectra calculations for all structure in figures. In the presented study, simulated systems of dyes are not covalently bonded with the silver surface.

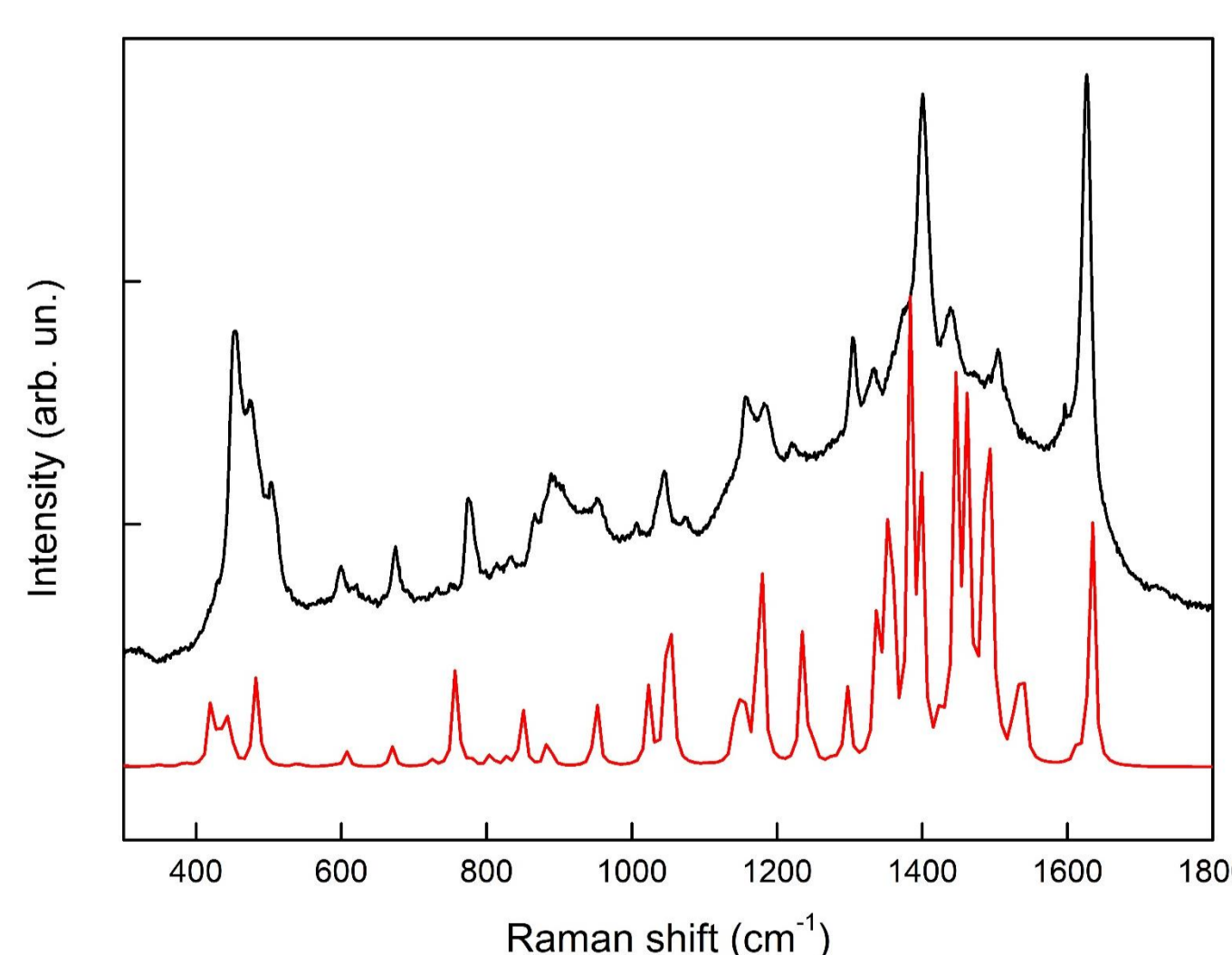
MB-systems



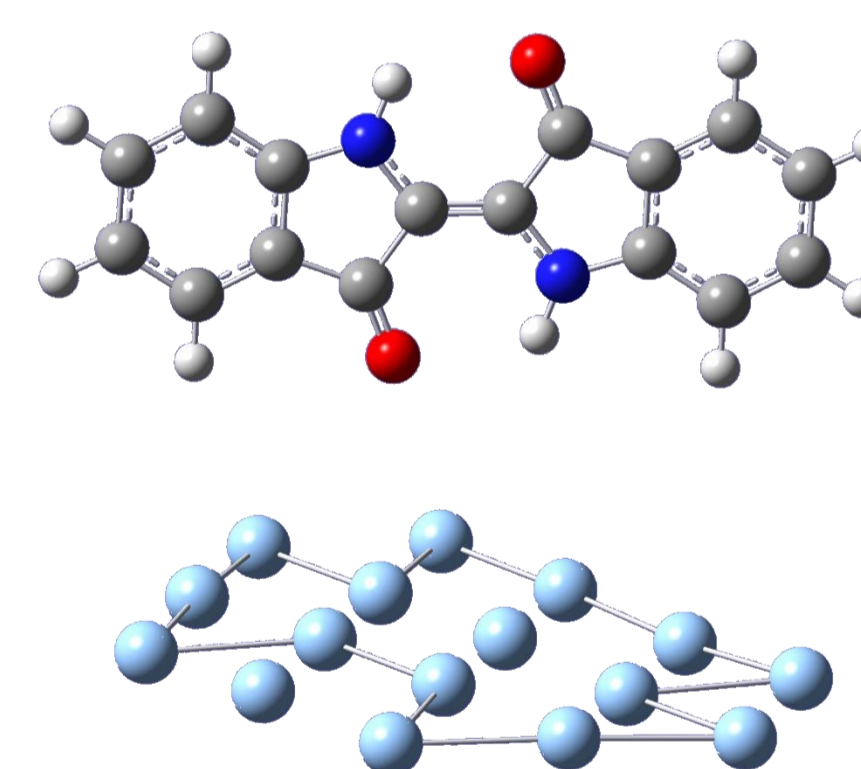
A



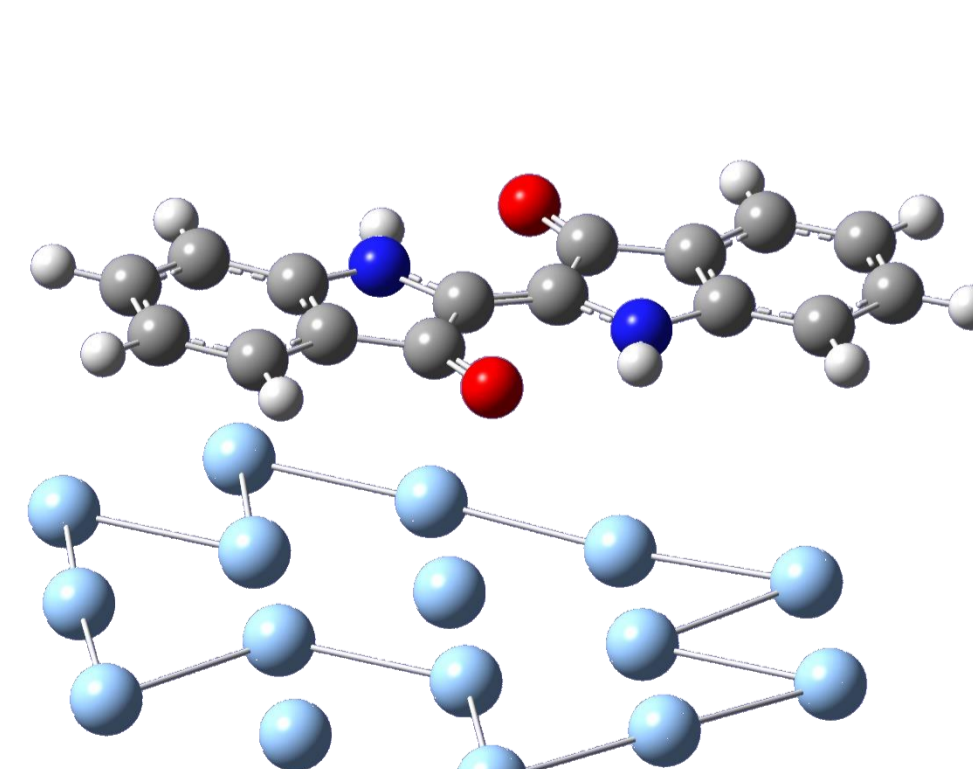
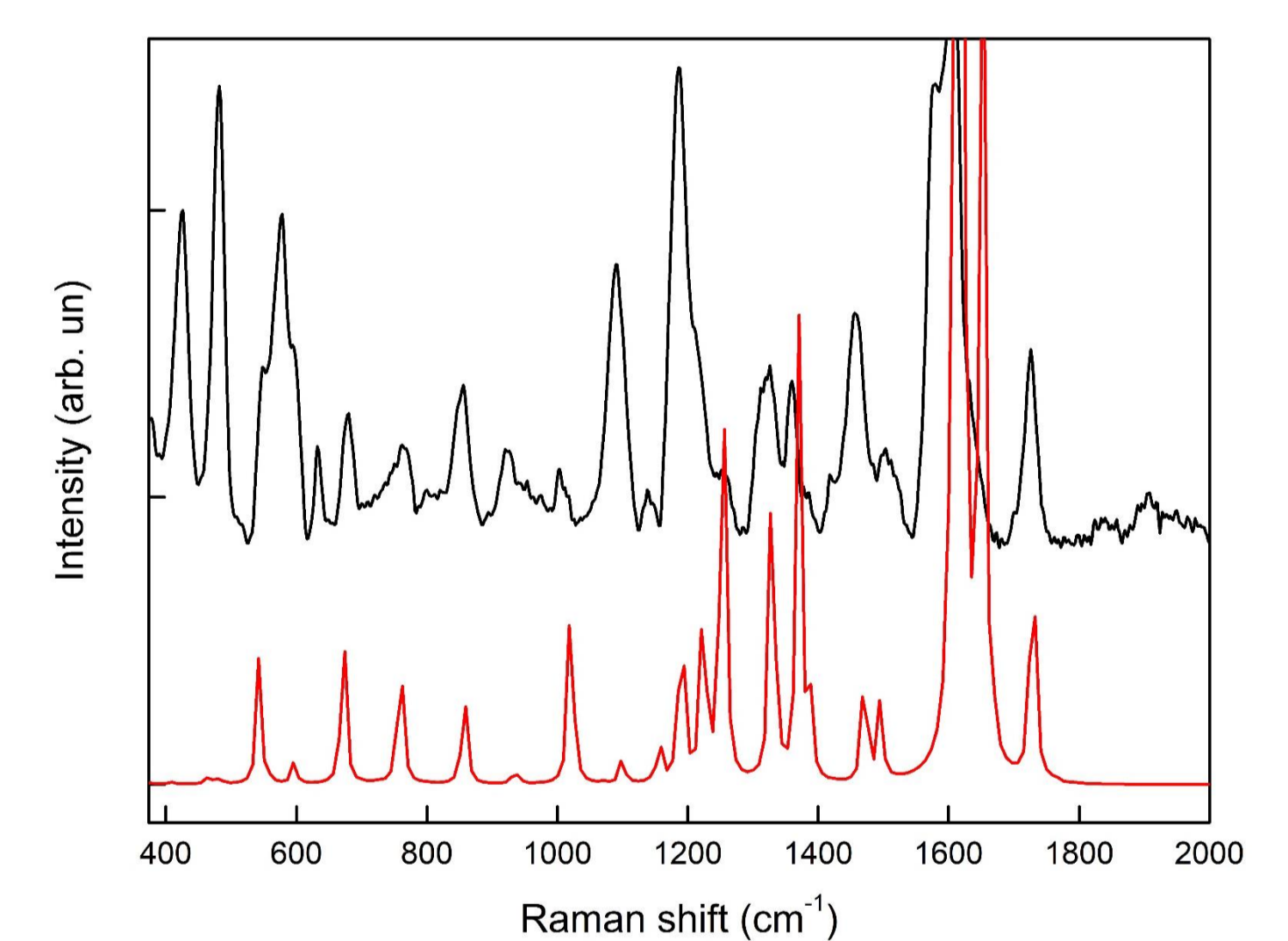
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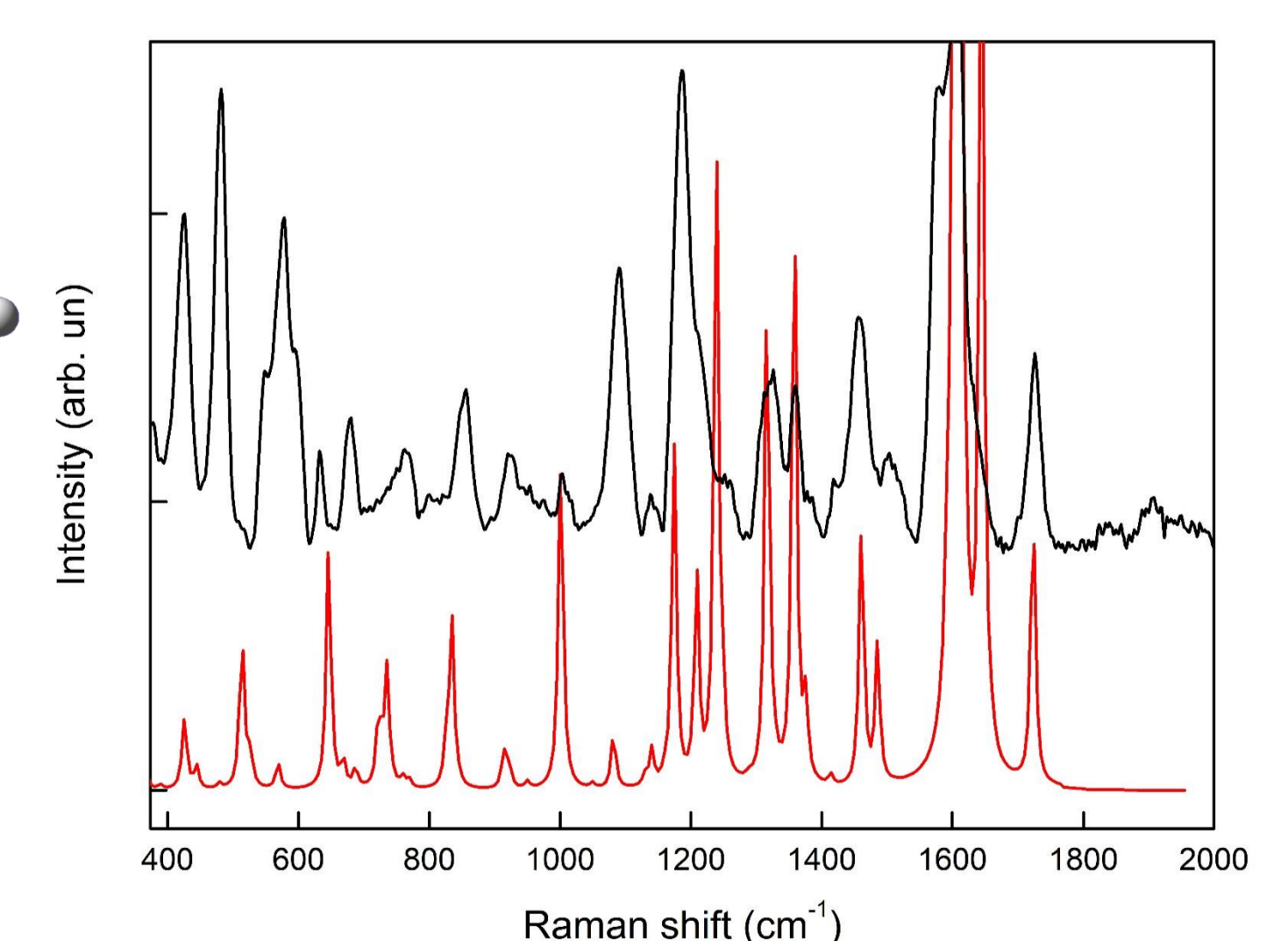
Indigo-systems



C



D



We report on DFT calculations for MB-Ag (A) and MB-Ag₂ (B) systems in comparison with SERS spectrum of MB solution 10^{-6} M. Raman spectra: black curve SERS experimental, red curve DFT Raman. We note that there is a good agreement between DFT calculations and experimental SERS spectra. More specifically, the MB-Ag₂ structure gives a better agreement with the experiment with respect to MB-Ag.

Perpendicular (C) and parallel (D) Indigo-Ag₁₆ complex optimized structure. The distance of the molecule from to the Ag surface is about 4 Å. Raman spectra: black curve SERS experimental, red curve DFT Raman. In this case for indigo dye the structure with 16 Ag atoms gives a better description between experimental and theoretical results with respect to structures where only one or two silver atoms are attached to the indigo molecule.

[1] E. Van Elslande, S. Lecomte, A. Solen Le-Ho, J. Raman Spectrosc. 39 (2008) 1001.

[2] E. Fazio, F. Neri, P. M. Ossi, N. Santo, S. Trusso, Appl. Surf. Sci. 255 (2009) 9676.

[3] V. Mollica Nardo, F. Aliotta, M. A. Mastelloni, R. C. Ponterio, F. Saija, S. Trusso, C. S. Vasi, Acc. Pei. dei Pericolanti 95 (2017) 1.

[4] V. Mollica Nardo, A. Sinopoli, L. Kabalan, R.C. Ponterio, F. Saija, S. Trusso, Spectr. Acta Part. A 205 (2018) 465.