

## SURFACE-ENHANCE RAMAN SCATTERING (SERS) OF HERBICIDE DIQUAT ON SILVER NANOSTRUCTURES

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Diquat (N,N'-Ethylene-2,2'-bipyridylum, DQ) dibromide is a non-selective herbicide and plant growth regulator, related structurally to paraquat, normally used in agricultural practices, which may cause moderate hepatic and renal toxicity [1]. In addition to this, DQ has shown an interesting electrodynamic activity with possible applications in supramolecular surface covering and functionalization useful in the detection of pollutants. However, DQ has been poorly characterized so far by spectroscopic methods. Surface-enhanced Raman scattering (SERS) is a very sensitive technique for the detection of this kind of molecules and in this study it is used to analyse the behaviour of this molecule in the presence of silver nanostructures.

The Raman scattering of a compound (or ion) adsorbed on or even within a few Angstroms of a structured metal surface can be  $10^3$ - $10^6$  greater than in solution [2]. This SERS effect is strongest on silver, but is observable on gold and copper as well. This phenomenon arises essentially from two mechanisms: an enhanced electromagnetic field produced at the surface of the metal and the formation of a charge-transfer complex between the surface and the molecule.

In the first case the intensity of the surface plasmon resonance of the metal depends on many factors including the wavelength of the incident light and the morphology of the metal surface [3]. The role of these nanostructures is correlated with the mechanism involved in the SERS enhancement, being essential the formation of surface nanostructures to induce a huge intensification of Raman emission through localized plasmon resonance in order to obtain high quality SERS spectra (**Figure 1**). In this work we have studied the influence of different excitation wavelengths and the morphology of the metal surface on the SERS spectrum of DQ.

Moreover, we present a Raman study of DQ consisting in a normal modes DFT calculation (**Figure 2**), as well as the normal Raman and SERS on Ag colloid and electrode. We have investigated the influence of anions ( $\text{Br}^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ) and the herbicide concentration on the adsorption mechanism onto the metal surface metal nanoparticles.

The SERS spectra obtained on Ag electrode shows two different spectral pattern depending on both applied potential and excitation wavelength. We think that the reduction of diquat onto the surface electrode occurs in the same way as some processes which give rise to adsorption-nucleation peaks as heptyl viologen on polycrystalline silver electrode [4] and it is also strongly related to the electrochemical reduction process of lucigenin molecule on Ag electrode [5].

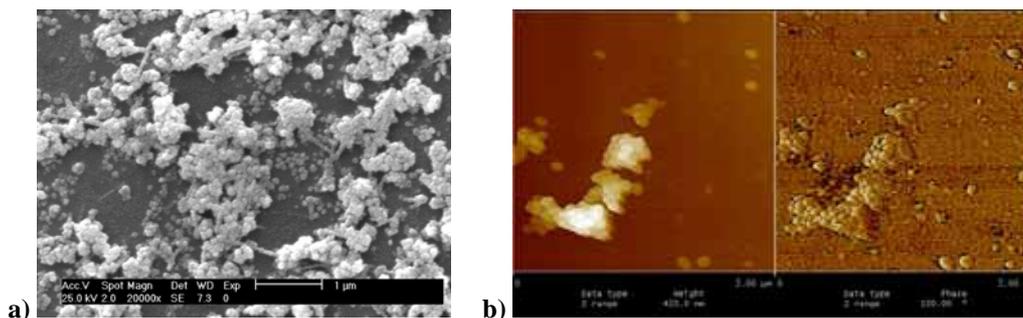
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### Figures:

**Figure 1.** SEM (a) and AFM (b) images of a silver colloid which uses citrate as reducing agent.



**Figure 2.** FT-Raman spectra of DQ: a) in solid state, b) in a 0.5 M aqueous solution and c) calculated spectrum of DQ at the B3LYP/6-31G\*\* level of theory.  $\lambda = 1064$  nm, a) 50 mW and b) 175 mW.

