# A combined study of the binding modes of Glyphosate on silver nanoparticles and implications for SERS

**Emonds-Alt G.**, Mignolet B., Malherbe C., Monbaliu J.C., Remacle F. and Eppe G.
G.EmondsAlt@ulg.ac.be, Department of Chemistry, University of Liège
Sart-Tilman, B6c, B-4000, Liège, Belgium

Laboratory of Inorganic Analytical Chemistry

## INTRODUCTION

In this **experimental-theoretical study**, we measured the SERS spectra of glyphosate. We investigated the effect of external factors affecting the SERS activity such as

- the pH
- the effect of competitor molecules blocking the access to the nanoparticle surface such as the stabilizing agent used to prevent the agglomeration of nanoparticles.
- the nature of the nanoparticle

The results are then rationalized with electronic structure computations carried out at the DFT level. We computed the **binding energies** and **Raman spectra** of several molecules (glyphosate, AMPA etc.) adsorbed on a silver cluster composed of 20 atoms.
By computing the Raman spectra of the glyphosate adsorbed on different binding sites and comparing them with the experimental SERS spectrum, we can determine the adsorption site of the molecule. In addition, we also computed the binding energies of the different molecules present in solution and by comparing these binding energies, we can determine if the stabilizing agent is blocking the access of the analyte to the nanorparticle surface.

## METHOD

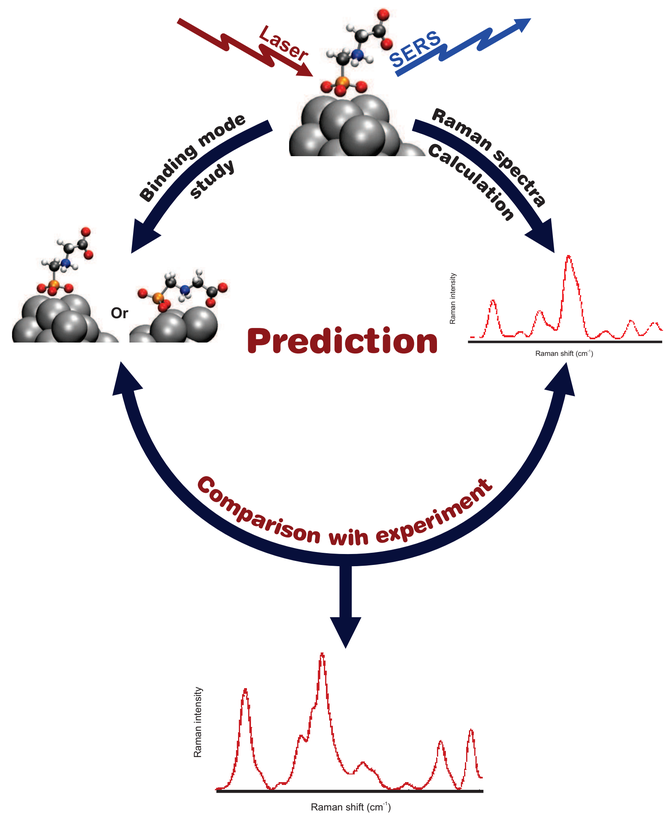


***Figure 1.*** *Representation of the method developed for this study. The comparison of the Raman spectrum, of an electronic structure of the glyphosate-$Ag_{20}$ complex, and the experimental spectrum gives information on the adsorption mode of glyphosate at the nanoparticle surface.*

## Adsorption modes

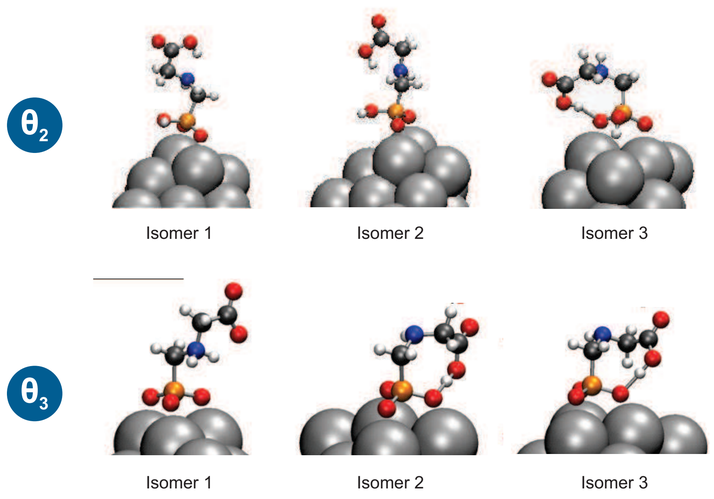


***Figure 4.*** *Equilibrium geometries of 3 different isomers of the monoanionic and dianionic glyphosate-$Ag_{20}$ complex.*

## EXPERIMENTAL DATA

### Effect of the pH on the SERS activity

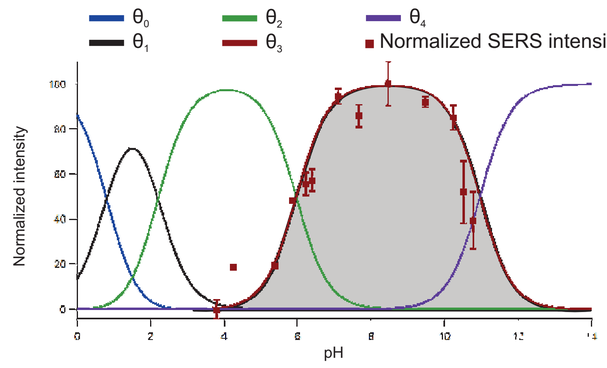


***Figure 2.*** *Fractional composition curves of the 5 forms of glyphosate in aqueous solution as a function of pH. The red dots represent the intensity of the SERS signal.*

## Binding energies

| | | Binding energy (kcal/mol) |
|---|---|---|
| $Ag_{20}$-glyphosate ($\theta_2$) | Iso 1 | 25.7 |
| | Iso 2 | 26 |
| | Iso 3 | 25 |
| $Ag_{20}$-glyphosate ($\theta_3$) | Iso 1 | 42.0 |
| | Iso 2 | 36.6 |
| | Iso 3 | 35.1 |
| $Ag_{20}$-Citrate | Ox | 46.6 |
| | Red | 60.1 |
| $Ag_{20}$-$(H_3BO_3)_3$ | | 30.0 |

***Table 1.*** *Adsorption energies ($E_{Ag20}$+$E_{Analyte}$-$E_{complex}$) of different molecules on the silver cluster surface.*

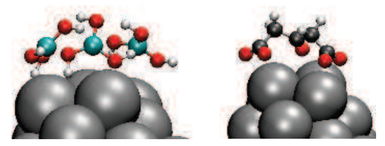

***Figure 6.*** *Equilibrium geometries of the complex $Ag_{20}$-$(H_3BO_3)_3$ (left) and $Ag_{20}$-citrate (right).*

## Computed Raman spectra

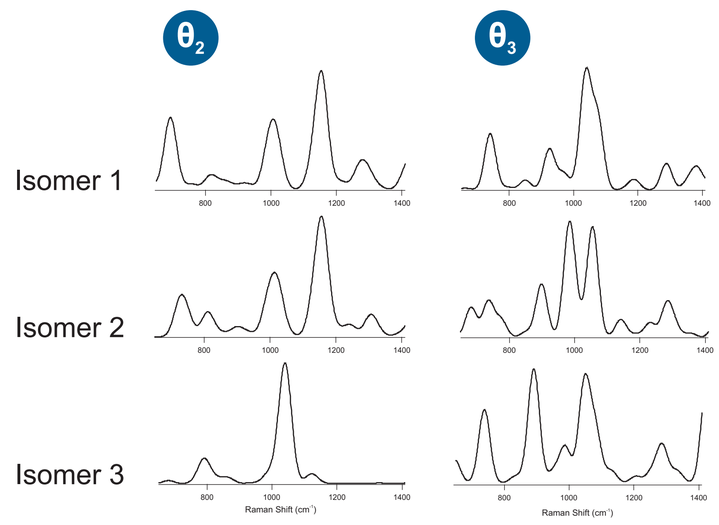


***Figure 5.*** *Raman spectrum of the 3 complexes presented in the adsorption modes section. Left $Ag_{20}$-Glyphosate ($\theta_2$) and right $Ag_{20}$-Glyphosate ($\theta_3$).*

## Effect of the nanoparticles stabilizing agent on the SERS activity

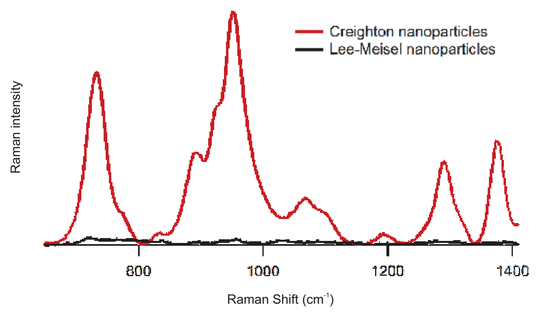


***Figure 3.*** *SERS spectrum of glyphosate with silver nanoparticles synthesized according to Creighton's protocol (Red) or Lee-Meisel's protocol (Black).*

## Chemical environment

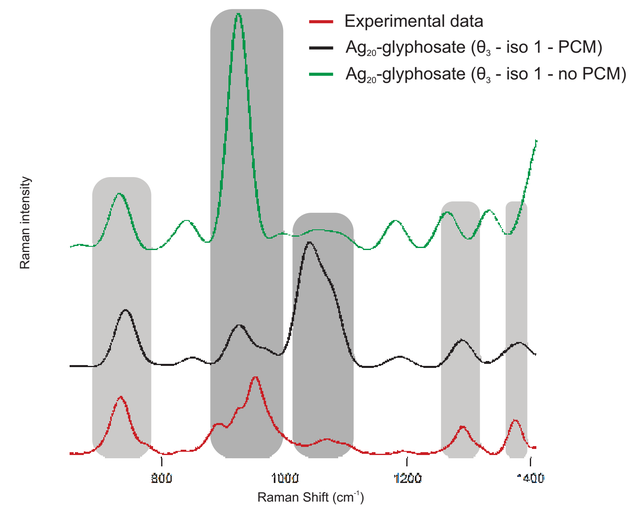


***Figure 7.*** *Raman spectrum of the complexes: $Ag_{20}$-Glyphosate ($\theta_3$ - iso 1 - no PCM) (Green), $Ag_{20}$-Glyphosate ($\theta_3$ - iso 1 - PCM) (Black) and experimental SERS spectrum of glyphosate at pH = 8 (Red).*

## CONCLUSION

**Form Experimental data**

- Glyphosate has more affinity for silver nanoparticles synthetized by the Creighton protocol.
- The dianionic form of Glyphosate is the only SERS-active form on silver nanoparticles.

**From electronic structure computations**

- Molecular modeling allows to understand the interaction between Glyphosate and nanoparticles.
- Glyphosate is adsorbed on nanoparticles by the phosphonate function of the molecule.

***Both data sets lead to complementary conclusions. Hence, computation can be used to predict the response of some experimental parameters in order to improve the SERS activity of molecule-nanoparticles systems.***