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# SERS of Biological Materials. From Amino Acids to Human Tissues

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**Abstract** – Important improvements of rotator cuff tendons diseases resulted after shockwave treatment. Neo-angiogenesis stimulation and hypercelularization are bio-processes probably associated to structural aspects resulting from biochemical changes induced by shockwaves. To attempt an explanation of these bio-processes it is proposed to use Raman spectroscopy and Surface-Enhanced Raman Scattering (SERS). This challenge started by the construction of vibrational data bases of amino acids, selected peptides and proteins, and particularly collagen. Results concerning the arginine (R) amino acid interacting with metal surfaces (Fig 1.), and its driving action in the MRKDV peptide (Fig. 2) are discussed in this presentation.

Motivated by the improvements of rotator cuff tendons diseases after shockwave treatment we attempt a spectroscopic explanation of the observed neo-angiogenesis stimulation and hypercelularization bio-processes. The proposed spectroscopic tools are Raman and Surface-Enhanced Raman Scattering (SERS) [1]. In order to accomplish this challenge we started by the construction of vibrational data bases of amino acids, selected peptides and proteins, and particularly collagen. Besides others results for several amino acids, peptides and proteins already obtained in our laboratory, we focus this contribution to the arginine (R) amino acid interacting with metal surfaces (Fig. 1.), and its driving action in selected oligopeptides deposited on nanotructured surfaces (Fig. 2).

L-arginine (R) amino acid was structurally studied through its infrared, Raman and surface SERS spectra, and theoretical methods. Net charge and hydropathy index were used to predict the possibility into obtain its SERS spectrum in colloidal solution. The interpretation of the SERS data suggests that the arginine-silver surface interaction in a colloidal solution and in the case of the arginine coated by the metal is mainly verified through the argininium moiety. Theoretical calculations for a model of arginine interacting with an Ag cluster support the observed SERS results.

The MRKDV peptide structurally associated with an immunomodulatory protein, and model peptides ADEDRDA and LGRGISL were also studied by SERS and quantum chemical computations. Samples were photo stable when probed with laser lines at 514 and 633 nm. SERS spectra were obtained only by coating the solid peptides with metal colloids on a quartz slice, making possible to obtain high spectral batch to batch reproducibility. MRKDV SERS spectrum is dominated by signals coming from the guanidinium moiety of R; guanidinium is the intrinsic probe which drives the orientation of the peptide on the metal surface. LGRGISL interacts with the metal surface through the guanidinium group and other terminal amino acid residues; a single structural conformation of the peptide on the surface is proposed. ADEDRDA interacts with the metal through various amino acid residues, also including the guanidinium moiety; at least two structural conformations seem to coexist on the surface. Similar theoretical calculations performed for R support the proposed experimental conclusions for the MRKDV peptide.

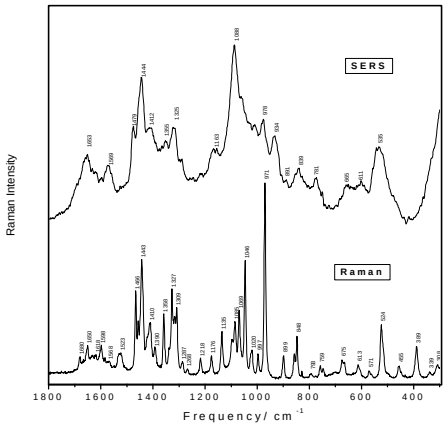


**Figure 1:** Raman spectrum of the solid arginine and SERS spectrum of arginine coated by Ag nanostructured.

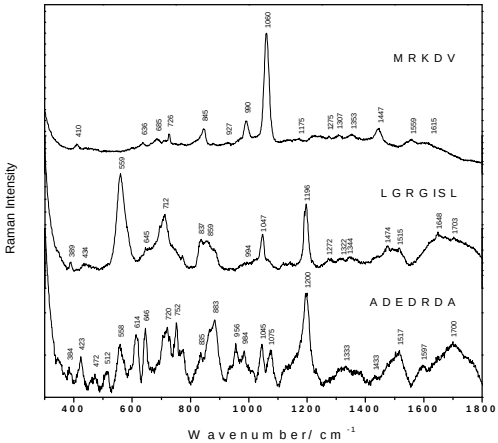


**Figure 2:** SERS spectra of oligopeptides MRKDV, LGRGISL and ADEDRDA.

[1] R. Aroca, *Surface-enhanced Vibrational Spectroscopy*. 2006, Chichester: John Wiley & Sons.