

SERS and quanta-mechanical calculations on autoassembling oligopeptides

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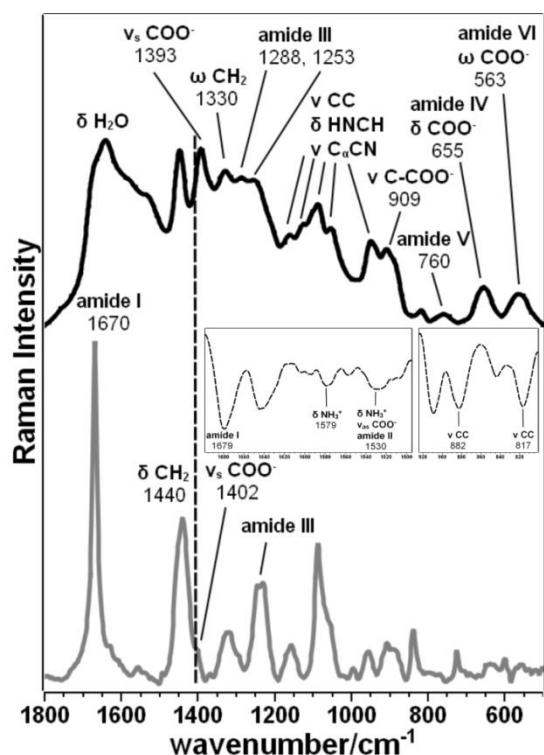
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Five alternating polar/non-polar peptides derived from the self-assembling peptide EAK-16 (AEAEAKAK)₂ were examined in comparison with the EAK-16 parent form (pept1). The peptides were studied for their possible use as biomimetic materials [1] due to their auto-assembling properties and to the presence, in two of them, of the RGD sequence, an active modulator of cell adhesion. The use of SERS allows the detection of peptides at very low concentrations (10⁻⁵-10⁻⁶ M), a feature of extreme interest to check their presence in the aqueous environment surrounding a metal implant and to study the effects of systematic amino acid substitution along the peptide chain on the corresponding interaction with the Ag colloidal nanoparticles. Quantum-mechanical data on two of the examined peptides were carried out and were very useful for clarifying the bands assignment debated in the literature. The results indicate that, in general, the peptide-nanoparticle interaction takes place through the carboxylate groups. As an example, the SERS spectrum of pept1 at 10⁻⁵ M concentration is reported in figure 1 in comparison with its spectrum in solid form.



The SERS spectrum displays an enhancement of the bands attributed to carboxylate vibrations, indicating that these groups directly interact with the nanoparticles. The most prominent band of carboxylate groups appears at 1393 cm⁻¹ (ν_s COO⁻), intensified and red shifted of about 10 cm⁻¹, as compared to the FT-Raman spectrum. This effect can be attributed to the proximity of the COO⁻ group to the surface and to a charge transfer mechanism [2]. Moreover, other bands can be attributed to COO⁻ vibrations: 909 cm⁻¹ (ν C-COO⁻), 655 cm⁻¹ (δ COO⁻) and 563 cm⁻¹ (COO⁻ wagging) [3]. The theoretical calculations pointed out that the last two bands are mixed with amide motions.

As regards the other examined peptides, the spacer substitution in the sequence is a factor able to affect the peptide-Ag particles interaction: the increase in the hydrophobic chain length (Ala substituted by 2-aminobutanoic acid) favors the interaction by NH₃⁺ groups, although the charge transfer interaction with the COO⁻ ions is still the main interaction with the colloid. In fact, the presence of many SERS bands attributable to the NH₃⁺ moieties of the Lys amino acid side chains, indicates the existence of interactions between the NH₃⁺ groups and the nanoparticles, mediated by the Cl⁻ anions present in the colloidal solution. The substitution of Ala with an aromatic Tyr residue strongly affects the interaction mechanism: the Tyr residue lies in a position close to perpendicular to the silver surface, partly as tyrosinate ion.

Figure 1 - Pept1: SERS spectrum in solution (black) and normal Raman spectrum of the solid (grey) in the 1800-500 cm⁻¹ region. In the insets: 2nd derivative spectrum of SERS spectrum of the 1700-1500 and 920-800 cm⁻¹ regions.

References

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