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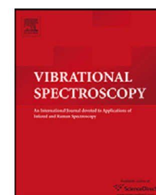

Surface enhanced Raman scattering study of L-lysine

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ABSTRACT

Different SERS spectra of lysine (Lys) in Ag colloidal surface were obtained. No identical SERS spectra of Lys were observed after a stabilization period, suggesting that a unique conformation and orientation on the metal surface of lysine do not exist at neutral pH. In general, Lys molecules interact with the surface through both the carboxylate and amino groups; the aliphatic moiety is close to the surface. The interpretation of the experimental results is supported by theoretical analysis of the molecule on the silver surface.

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1. Introduction

Amino acids are the molecular basis of proteins and enzymes. There is a varying number of amino acid residues required to make up different proteins. Vibrational studies on biological materials, in particular those related with surface enhanced Raman scattering SERS, have been intensively developed in the last 10 years. SERS substrates provide an innovative and powerful approach to protein and amino acid studies [1]. The resultant SERS spectrum of a protein represents the point of interaction with the metal, influenced by all the amino acids. To interpret this composite spectrum, it is necessary to have a fundamental understanding of the interactions of individual amino acids and peptides with the metal substrates. Important advantages offered by SERS are the use of small quantity of sample, detection of very low concentration and use of low laser power. The most relevant characteristic inherent to the Raman spectroscopy is the insignificant Raman cross-section of water, which allows study biological materials in their natural media. Lysine is an amino acid showing 2.2, 9.0 and 10.5 values for pK_a; this fact suggests the importance into select the pH range for any spectroscopic study in solution. Raman and SERS studies on L-lysine (Lys) have been published. Xu et al. [2] from the Raman spectrum found that Lys molecules in the peptide Lys-Lys are adsorbed onto a Au colloid surface through the ε-amino group. It has been reported from SERS measurements [3] that Lys interacts with a Au colloid at pH 10.8 through the ionized ε-amino group; the electrostatic interaction between the positive charge of the NH_3^+ group and the negative charge of the gold surface is one of the most important factors that determine the intensities of the SERS signals.

Stewart and Fredericks [4] showed that adsorption of 19 L-amino acids was via the ionised carboxylate group, and that the side chain of most of the molecules was also in close proximity to the surface; the spectra also indicated that, in contrast, the amine function was protonated and relatively far from the surface. Reyes-Goddard et al., [5] published a review on the photodiagnosis using Raman and SERS of bodily fluids, including a section on amino acids based solutions. From these works one can deduce that the SERS spectrum of Lys depends on several factors such as laser line, the physical chemistry characteristics and the nature of the metal substrate, pH, ionic strength and concentration of the solution, aggregation time, and the eventual chemical reaction between the amino acid and the metal surface. The SERS spectrum reflects those mechanisms involved in the spectral enhancement, electromagnetic (EM) and charge-transfer (CT) [6], and the organization and orientation of the analyte on the metal surface. We have recently carried out a SERS study of L-tryptophane Trp [7]; we concluded that a unique SERS spectrum of Trp, corresponding to the most stable conformation and orientation on the metal surface, is observed after a stabilization period. The observed spectra vary

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depending on both the preparation of the silver colloid and the aggregation time.

The present contribution deals with the SERS spectrum of Lys obtained under specific experimental conditions, particularly the time accommodation of the analyte in a silver colloidal solution at neutral pH. We also perform calculations on a simplified molecular model in which Lys interacts as zwitterionic species with a large silver surface. To our knowledge no calculations in this sense for lysine have been performed.

2. Experimental

2.1. Materials

Lysine of analytical grade was purchased from GIBCO and used as received. Stock solutions of lysine in water were prepared to a final concentration of 10^{-3} M. Aqueous stock solutions of the compounds were prepared in nanopure water.

2.2. Sample preparation

Colloidal silver nanoparticles were prepared by using hydroxylamine hydrochloride as reducing agent [8]. These nanoparticles have the advantage of a more uniform distribution of size and shape together with the absence of interferences from remainder oxidation product.

Samples for SERS measurements were prepared by adding 10 μL of the lysine solution to 1000 μL of the silver colloid. Final solution at a concentration 1.4×10^{-5} M was obtained at pH 7 by adding drops of an aqueous solution of HCl. From an analytical viewpoint and on the basis of the pK_a values, one could expect that the NH_3^+–$(CH_2)_4$–$CH(COO^-)NH_3^+$ species be predominant at the mentioned amino acid concentration.

An aliquot of the original non-activated colloid was placed on a glass slide with a shallow groove, and then the cover glass slide containing the dried activated Ag nanoparticles was placed on the groove with the side containing the dried nanoparticles facing downwards so that the suspension is placed in the groove [9]. Only sample monolayers were assumed to contribute to the SERS spectra.

Scanning at room temperature was performed for a unique sample at several times, from 30 min to 12 h.

2.3. Instrumentation

The micro SERS spectra were recorded with a Renishaw Raman RM1000 equipped with the 514 nm laser line, an electrically refrigerated CCD camera, and a notch filter to eliminate the elastic scattering. The spectra shown here were obtained by using a 50-mm length lens. The output laser power on the sample was about 0.2 mW. Spectral resolution was 4 cm^{-1}. The spectral scanning conditions are chosen to avoid sample degradation. Spectra reported are single scans.

2.4. Spectral reproducibility

The SERS spectra from cast colloids taken after a short period of aggregation show a variable spectral pattern, an indication of several molecule–surface interaction sites. Each one of the different spectra of Lys in the silver colloid at the different hours is reproduced from batch to batch.

3. Molecular models, methods and calculations

The 320 silver atoms surface was the same employed in our previous studies on nanotubes [10] and tryptophane [7]. We modeled Lys as a zwitterion with the N atom of the alkylic side chain protonated as it is expected at pH 7. Molecular Mechanics was employed to optimize Lys geometry. This is because we expect normal bond lengths and angles. To build the Lys-Ag layer system we proceed as follows. Keeping fixed the Ag bilayer, we employed Molecular mechanics to optimize the Lys-Ag geometry. Lysine was placed at different distances and orientations from the center of the Ag bilayer. Fig. 1 shows the final geometry of the system. Extended Hückel theory (EHT) was used to calculate the wave function of the isolated Lys and the Lys-Ag system. The Hyperchem program was used [11]. EHT calculations produce qualitative or semiquantitative descriptions of molecular orbital and electronic properties. Also, it was shown that, within the Hartree–Fock–Rüdenberg picture, EHT is compatible with the non-empirical Hartree–Fock method in Roothaan's form [12]. The combination of EHT with molecular mechanics was able to give, for example, a qualitative explanation of our previous work in nanotubes [10] humic acids [13] and tryptophane [7].

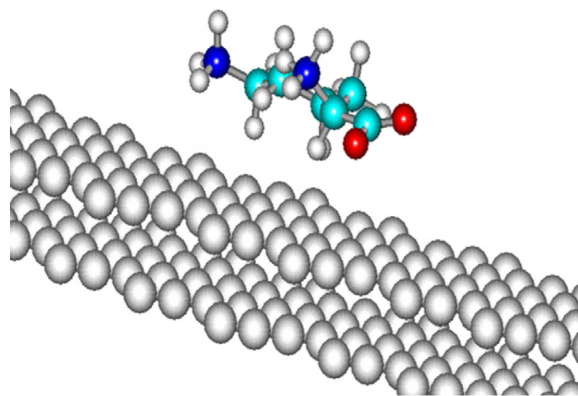

Fig. 1. Final geometry of the lysine-Ag system.

4. Results and discussion

4.1. Raman spectra

The Raman spectrum of the lysine salt in the solid state is displayed in Fig. 2. The band assignment is performed on the basis of published data on related molecules [14–18] and general characteristic group frequencies [19].

A large and intense band at about 3180 cm^{-1} belonging to the stretching α- and ε-amino groups is better observed in the infrared spectrum. The Raman spectrum shows a group of characteristic hydrocarbon aliphatic stretching bands at 2987, 2959, 2908 and 2870 cm^{-1}. Bands at 1621 and 1576 cm^{-1} could be ascribed to a asymmetric stretching of the COO^- group. The group of five bands from 1480 to 1421 cm^{-1} with a maximum at 1440 cm^{-1} are assigned to deformations of NH_3^+ species. The asymmetric band at 1306 cm^{-1} is the most intense in the group of lines in the range 1306–1360 cm^{-1}; they are assigned to NH_2 and CH_2 bending modes coupled to CH_2 twisting vibrations. The fact that we observe several bands in those regions could be associated to the coexistence of different aliphatic chain conformers. The symmetric νCOO^- modes are also expected in those regions. Bands between 1100 and 1250 cm^{-1} are mostly NH_2 twisting modes. The aliphatic skeletal stretching vibrations νCN and νCC are observed in the region 860–1100 cm^{-1}; the νC–COO^- mode is expected around 930 cm^{-1}. At least three bands below 800 cm^{-1} at 705, 550 and 473 cm^{-1} could be assigned to different deformation modes of the COO^- group.

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