SERS and theoretical studies of arginine

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ABSTRACT

Arginine amino acid (Arg) has been vibrationally studied through its infrared, Raman and surface-enhanced Raman scattering (SERS) spectra, and theoretical calculations. Net charge is used to predict the possibility to obtain the SERS spectrum of Arg in colloidal solution. The interpretation of the SERS spectral data suggests that the Arg–Ag nanoparticles interaction in a colloidal solution and in the case of the Arg coated by Ag is mainly verified through the guanidinium moiety. Theoretical calculations performed by using extended Hückel theory method for a model of Arg interacting with an Ag cluster support the observed SERS experimental result.

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1. Introduction

The Raman spectral signal intensity is dramatically enhanced from a determined adsorbate–substrate interaction, giving rise to the surface-enhanced Raman scattering (SERS). SERS has been an active research area with important applications ranging from surface chemistry to biological chemistry and biomedical analysis [1]. SERS of biomolecules such as cells, DNA, proteins, peptides and amino acids, has been reported. Wei et al. [2] reported that the SERS spectra of proteins and DNA are difficult to reproduce and interpret. Batista et al. [3] recently published results showing that SERS substrates prepared using polycarbonate membranes as templates for gold deposition are promising for the fabrication of planar SERS platforms for analytical/bioanalytical applications. Seballos et al. [4] pointed out the importance to understand the binding mechanism between the various monomer units of a peptide interacting with a nanostructured metal surface. On this basis one could expect to develop optimal conditions for the analyte and metal substrate preparation. In this perspective several works concerning SERS studies of simple amino acids and small peptides have been conducted [2,4–10]. We have recently described the lysine [5], tryptophan [6] and cysteine [7] metal surface interaction by using SERS spectra and theoretical calculations. The present vibrational study involves the arginine (Arg) free and interacting with

Ag nanoparticles (NPs). DiCostanzo et al. [11] described the implications of the arginine–metal interactions in the structure and function of proteins. Vijayakumar et al. [12] registered the Raman and IR spectra of arginine–nitrate hemi-hydrate performing a complete band assignment supported by HF/6-31G(d) calculations. Petrosian and Sukiasyan [13] studied by ATR and Raman crystals of Arg·HNO$_3$·0.5H$_2$O and Arg·2HNO$_3$; a complete band assignment for both crystals was proposed. A temperature-dependent Raman study of arginine hydrochloride monohydrate single crystal was performed by Lima et al. [14]; a phase transition was identified and several spectral changes with the temperature were associated to hydrogen bonding involving the t(NH$_2$) and r(NH$_3$$^+$) deformation modes. Raman bands of arginine were published by DeGelder et al. [15] in a large Raman study of biologic materials. Wolpert and Hellwig [16] published the IR spectrum of several amino acids in solution, including arginine; the band assignment is proposed for arginine at controlled pH equal to 6.7. IR and Raman spectra of (C$_6$H$_{16}$N$_4$O$_2$$^{2+}$·2NO$_3$$^-$) crystal were studied and the observed IR and Raman lines were assigned by Ramaswamy et al. [17]. Observed changes in the position and intensity of several bands are ascribed to extensive intermolecular hydrogen bonding in the crystal. Spectra show that the carboxyl group forms a strong hydrogen bond whereas the nitrogen atoms of the amino and guanidyl groups of the cation form normal hydrogen bonds with the oxygen atoms of the anions. Despite of the complete reported data there still exist controversies into the band assignment in particular vibrations concerning the guanidinium group of arginine. IR and Raman spectra and Density Functional Theory (DFT) data on N,N′-diphenyl

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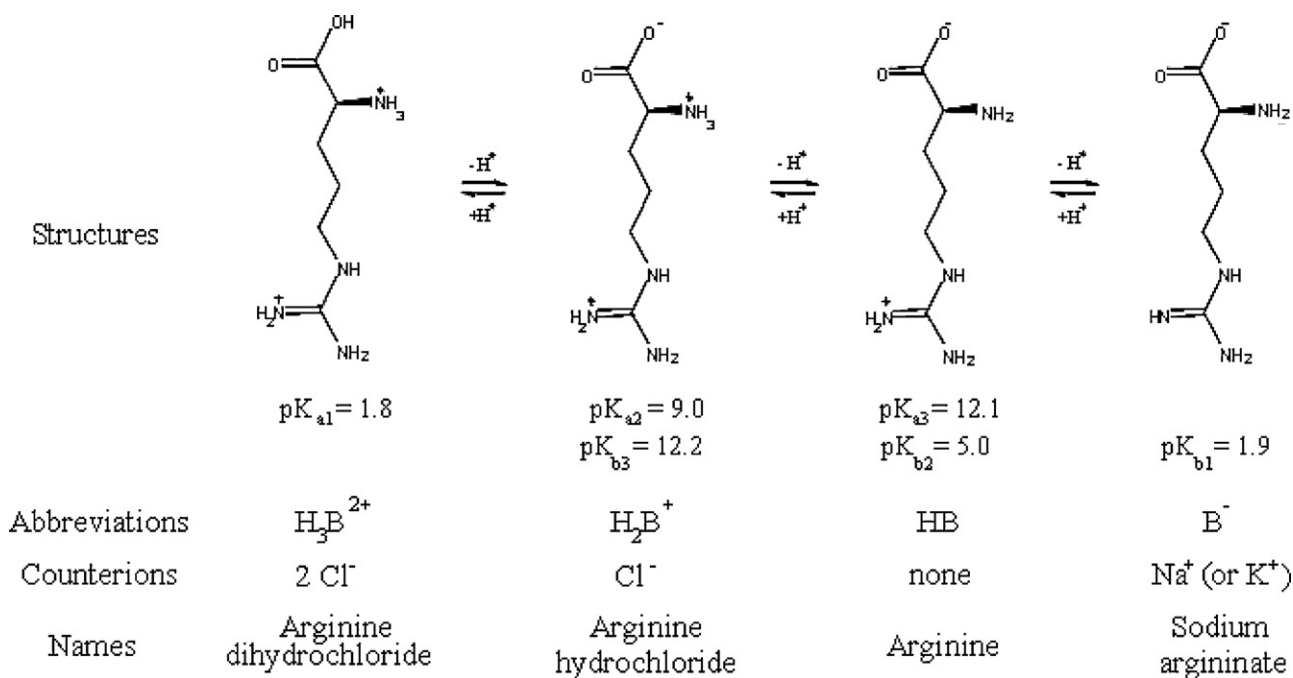 *E-mail address:* facien05@uchile.cl (M.M. Campos-Vallette).

Fig. 1. Structures and pK$_a$ values for arginine.

guanidinium oxalate crystals were reported by Binoy et al. [18]. Other guanidinium band assignments are proposed by DiCostanzo et al. [11] in the study of the stereochemistry of guanidine–metal interactions, and by Zawadzki [19], who described the synthesis and spectral studies of gold (III) complexes with guanidine derivatives.

Different structures for arginine predominate at specific pH ranges as displayed in Fig. 1. At low pH the α-amino and α-carboxyl groups are protonated, and the positively charged guanidinium group is in its protonated form. The increasing pH converts some of the H$_3$B^{2+} to H$_2$B$^+$ species. The carboxyl and carboxylate forms are in equilibrium when pH = pK$_{a1}$. The concentrations of the other forms are negligible. At the first equivalence point the intermediate species is the predominant one, with smaller (and approximately equal) amounts of H$_3$B^{2+} and HB. On the other hand, the net charge of arginine is useful to predict the possibility to obtain the SERS spectrum. In the present case the positive net charge by itself of the H$_2$B$^+$ species, predominant at pH close to 7, should drive the orientation of the amino acid to the metal surface, thus displaying a SERS spectrum in a metal colloidal solution. To our knowledge works in this perspective have not been published. Thus, in order to verify that proposition we have two goals. First, to obtain a reproducible SERS spectrum for the lowest analyte concentration, that is to determine the best conditions imposed by the metal surface physicochemical characteristics to improve the analyte–metal interaction. Second, on the basis of a complete vibrational IR and Raman bands assignment of the solid arginine and on its SERS spectrum we infer the analyte–metal surface interaction nature. In order to complete the analysis of the SERS experiments, a theoretical study based on the extended Hückel theory and 6-31G* methods for a simplified molecular model for the analyte–metal interaction is proposed.

2. Materials and methods

2.1. Sample

L-Arginine hydrochloride solid was supplied from Gibco and used as received. Stock solutions of Arg in water were prepared to a final concentration of 10^{-3} M. Aqueous stock solutions of the amino acid were prepared in nanopure water. pH close to 7 was reached by adding drops of NaOH solution; this condition guarantees the predominance of the H$_2$B$^+$ species, the most abundant in physiological conditions.

2.2. Preparation of silver nanoparticles

NPs were prepared by chemical reduction of silver nitrate with both trisodium citrate and hydroxylamine hydrochloride [20]. The resulting colloids display a final pH of 5.5 and near 7, respectively. The aqueous solutions utilized for the NPs formation were prepared by using triply distilled water. Colloids showed a milky grey colour. Also we prepared Ag island films from metal sublimation at both controlled rate and thickness.

2.3. SERS and Raman samples

10 μl of aqueous 10^{-3} M Arg solution was added to 500 μl of citrate and hydroxylamine reduced Ag colloidal solutions separately; a drop of each system was deposited onto a quartz slide. 10 μl of the aqueous 10^{-3} M arginine stock solution was deposited onto a quartz slide and dried at room temperature. Then, dried Arg sample was coated by adding 10 μl of hydroxylamine reduced Ag colloidal solutions. Likewise, 7 nm of Ag island film was sublimated onto the dried Arg at a rate of 0.3–0.5 nm/s. Room temperature analyte–metal system was used for the SERS measurements. Raman spectra were registered in solution and after water evaporation.

2.4. Instrumentation

Metal island films were prepared by using a Balzer evaporating system; thickness was monitored by an XTC Inficon quartz crystal oscillator. The IR spectrum of the solid in KBr disk, see Fig. 2, was obtained by using a Bruker Equinox 55 FTIR, equipped with a DTGS detector. The Raman of the solid, Fig. 2, and the SERS spectra of Arg (Figs. 3 and 4) were measured with a Renishaw micro-Raman system (RM2000) equipped with the 514 and 633 nm excitation laser
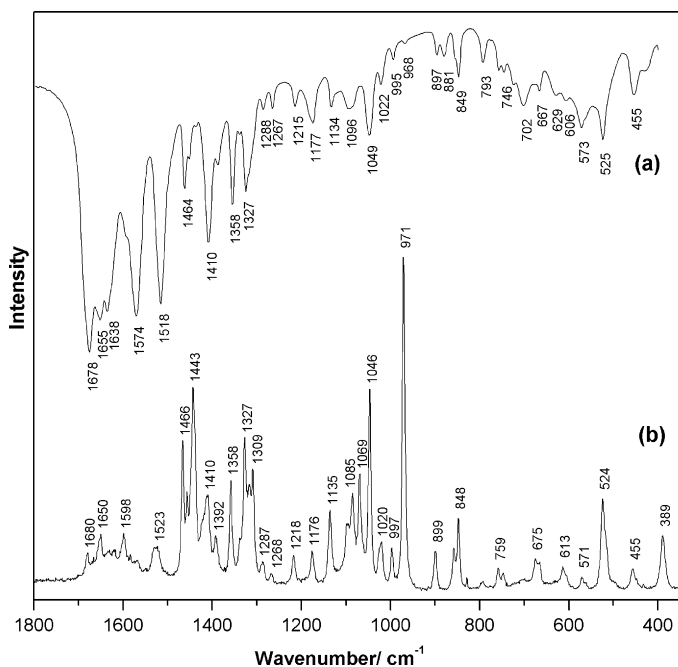
Fig. 2. Infrared (a) and Raman (b) spectra of solid arginine.

Fig. 4. SERS spectrum of dried arginine coated by silver nanostructured (a) and Raman spectrum of solid arginine (b).

lines, a Leica microscope and an electrically cooled CCD camera. The signal was calibrated by using the $520\,cm^{-1}$ line of a Si wafer and a $50\times$ objective. The laser power on the Arg–Ag system was less than 2 mW. The resolution was set to $4\,cm^{-1}$ and 1–20 scans of 10 s were averaged. Spectra were recorded in the 200–$4000\,cm^{-1}$ region. Sample was photo stable when probed with laser lines at 514 and 633 nm. The best spectral data were obtained by using the 633 nm laser line.
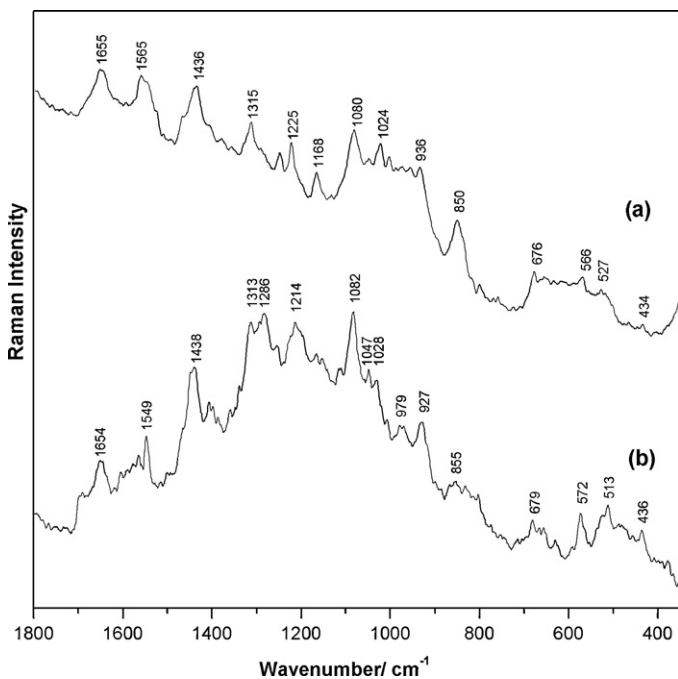

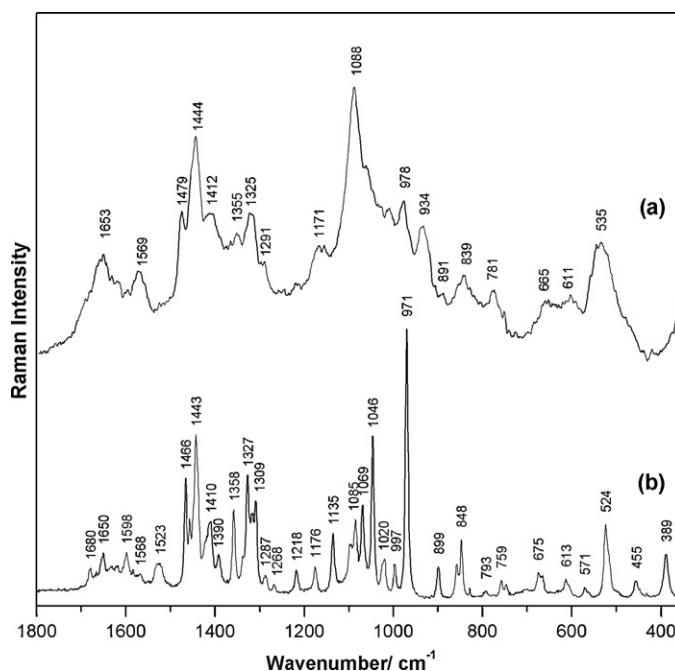**Fig. 3.** SERS spectra, (a) and (b), obtained by addition of the arginine solution to the colloid.

2.5. Spectral reproducibility

No reproducible SERS spectra were obtained by using the traditional way that is by addition of the sample solution to the colloidal suspension or the inverse. The SERS reproducible spectra from batch to batch were obtained by adding the Ag colloidal solution onto the dried Arg sample. We have also found the same reproducible spectra by fabrication of the NPs by metal sublimation onto the dried Arg sample. The conditions of the present samples (solid) avoid accomplishing a SERS study at different pH.

3. Molecular models and calculations

In order to complete the analysis of the SERS experiments, a theoretical study was performed. A simplified molecular model for the analyte–metal surface interaction is proposed. The silver atoms surface was the same employed in our previous studies [5,6,21]. Briefly, a face centred-cubic structure with $a = 0.408$ nm and $9 \times 9 \times 2$ cells was built and trimmed to get a planar double layer composed of 324 silver atoms. Arginine H_2B^+ species was modelled as a zwitterion.

Molecular Mechanics was employed to optimize both Arg (H_2B^+ species) and the Arg–Ag geometries. The bilayer geometry was kept constant. The Arg–Ag system was placed at different distances and orientations from the centre of the Ag bilayer. Fig. 5 shows the final geometry for Arg–Ag system.

Extended Hückel theory (EHT) was used to calculate the wave function of Arg as isolated system, and interacting with the Ag surface. The Hyperchem program was used [22]. The EHT calculations produce qualitative or semi-quantitative descriptions of molecular orbital and electronic properties [23]. The combination of EHT with Molecular Mechanics was able to give, for example, a qualitative explanation of our previous SERS works in lysine [5], tryptophan [6], nanotubes [21] and humic acids [24], and interacting with Ag surfaces.
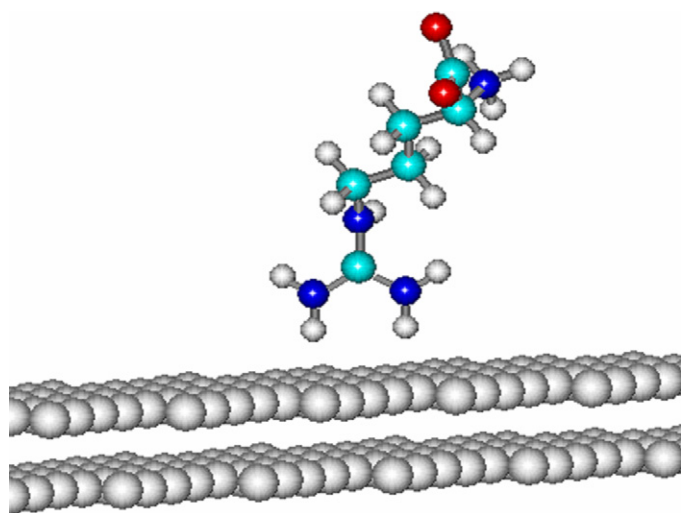
Fig. 5. Predicted molecular model for the arginine silver surface interaction.

4. Results and discussion

4.1. Physicochemical properties of arginine

Fig. 1 contains the different chemical structures and the corresponding pKs of Arg at several pH conditions. From the net charge value it is possible to infer about an eventual Arg–Ag interaction in colloidal solution; that is, the positive charge on arginine H_2B^+ species could induce an analyte–metal interaction. The interaction should take place through the guanidinium group. On the basis of these features one should expect to observe a SERS spectrum in Ag colloidal solution for Arg. This hypothesis was confirmed. In fact, it was possible to obtain more than one SERS spectrum for the H_2B^+ species in the citrate and hydroxylamine reduced Ag colloidal solutions. Fig. 3 displays two of the hydroxylamine reduced Ag colloidal spectra. Despite of the high hydrophilicity index for Arg (3) [25], suggesting a tendency to remain in the solution, it is the net charge which definitively drives the orientation of the amino acid to the metal in the colloidal solution. The negative charge on the metal surface guarantees the colloid stability and the strength of the analyte–metal interaction, this is related to the different energy necessary for inducing a charge transfer process between the metal and the adsorbate [26]. Then, in order to obtain a net analyte–metal interaction the hydrophilicity index and the net charge of the amino acid should be considered.

4.2. Infrared and Raman spectral analysis

IR and Raman spectra of solid Arg are displayed in Fig. 2. The spectral analysis was performed on the basis of published results on several amino acids [5–7,27,28] including Arg [12–17] and from data on related molecules [29]. The analysis considered the most current assignment proposed by the different authors. However, in some cases is noted some difference in the assignments due to distinct crystallographic space groups. The most probable band assignments are displayed in Table 1. NH$_2$ scissoring deformation modes appear in the 1638–1574 cm^{-1} region with strong intensity in IR and weak relative intensity in Raman. Characteristic IR bands below 1700 cm^{-1} are due to the asymmetric stretching of COO$^-$ and deformations of the NH$_2$ and NH$_3^+$ groups. CH$_2$ deformations display more intense bands in the Raman spectrum than in IR. At least three stretching CN vibrations (C=N and C–N) for single charged arginine with different counter ions are expected in the IR 1652–1693 (νC=N), 1618–1663 (νC=N) and 1176–1183

(C–N) cm^{-1} spectral region. Further, the NH$_3^+$ asymmetric deformation can be found at about 1600 cm^{-1}, while the symmetric modes are located ca. 1520 cm^{-1}. These bands are broad and intense. A NH$_2$ rocking vibration is observed at about 1140 cm^{-1}. In the IR and Raman spectra bands in the 1049–1096 cm^{-1} range are ascribed to νC–N. The medium strong Raman band at 1046 cm^{-1} is assigned to ωNH$_3^+$; the corresponding signal in IR is observed with medium intensity. The most intense band in Raman is observed at 971 cm^{-1} and corresponds to the ρCH$_2$ mode. The νC–C modes, medium in IR and weak in Raman, are expected in the 1000–800 cm^{-1} spectral range; NH wagging and torsion modes are located in the 850–720 cm^{-1} spectral range. Rocking CH$_2$ modes are considered below this range (760–712 cm^{-1}). Normal modes corresponding to COO$^-$ wagging and deformations have been assigned close to 670 cm^{-1}. At about 570 cm^{-1} rocking COO$^-$ has been pointed out in the literature. Raman bands associated with the NH$_2$ deformation vibrations are observed in the 480–595 cm^{-1} region. The strong absorption at 1046 cm^{-1} and the medium and weak ones at 1523, 848 and 793 cm^{-1} are ascribed to the guanidinium fragment according to different authors [4,10,11,15,18,19,29–32].

4.3. SERS spectra

A unique and reproducible SERS spectrum in colloidal solutions for Arg was not achieved. In Fig. 3 we display two SERS spectra of Arg in hydroxylamine Ag colloidal solution. This situation is probably due to the coexistence in solution at pH 7 of H_2B^+ and the less abundant species H_3B^{2+} and HB (see Fig. 1). Moreover, each one has several conformational possibilities originated on the aliphatic fragment. These structures should orientate differently on the metal surface, thus giving rise to different SERS spectra. A succeeding reproducible SERS spectrum was obtained only by coating the dried analyte with metal nanostructures; this spectrum resulted identical to that obtained by sublimating Ag on the dried Arg sample. SERS spectrum of Arg along with its Raman spectrum is displayed in Fig. 4. The Raman and SERS spectral profile is similar, with particular and delimited differences. Differences in the relative intensity and frequencies are related with vibrations associated to the chemical groups interacting with the metal surface [5,6]; this is the case for the guanidinium bands observed in Raman in the range 950–1100 cm^{-1}. Those bands far from the surface are expected to maintain their spectral characteristic, which is verified in the case of bands associated with the amino, and carboxylate moieties. The spectral analysis of the SERS data was performed on the basis of the present IR–Raman analysis and SERS band assignments of several amino acids [5–7]. Table 1 contains the most probable band assignment. The strongest band at 1088 cm^{-1} and those feeble at 839 and 781 cm^{-1} are ascribed to deformations of the (NH$_2$/NH$_2$)$^+$ guanidinium moiety. Thus, bands at 1653, 1569, 1444 and 1163 cm^{-1} belong to different deformation modes involving the NH bond. The medium/strong intensity of the band at 1444 cm^{-1} suggests that this vibration is close to the metal surface and thus could be assigned to a NH vibration of the guanidinium group. The weak bands at 1653, 1569 and 1163 cm^{-1} are ascribed to vibrations of the amino group of the amino acid terminal moiety. Vibrations of the aliphatic chain are assigned to the weak and medium bands at 1479, 1355, 1325, 993, 978, 934 and 891 cm^{-1}. The relative intensification of the 1327 cm^{-1} Raman band, assigned to ωCH$_2$ and the intensity decrease of the 971 cm^{-1} Raman band, attributed to ρCH$_2$ suggest a perpendicular orientation of the aliphatic chain respect to the surface. Finally, the weak bands at 1412, 665 and 611 cm^{-1} and the multiple medium one at 535 cm^{-1} are assigned to different vibrations of the carboxylate group. On the basis of this spectral interpretation it is possible to propose that the guanidinium moiety drives and deter-

Table 1
Raman, infrared (IR) and SERS frequencies (cm^{-1}) of arginine, and the most probable band assignments.

Raman	IR	Most probable assignment	SERS	Most probable assignment[a]
1680 w	1678 s	ν_{as} COO$^-$, δ_{as} NH$_3^+$, ν_{as} C=N		
1650 w	1655 s	δ NH$_2$, ν C=N	1653 m	def. NH (TF)
	1638 ssh	ν COO$^-$, scis. NH$_2$, ν C=N		
1598 w		δ_{as} NH$_3^+$, δ NH$_2$		
	1574 s	scis. NH$_2$	1569 m	def. NH (TF)
1523 wm	1518 s	δ_s NH$_3^+$, δ CNH, ν C–N, ν_{as} COO		
1466 m	1464 mw	ip δ CH$_2$	1479 w	def. CH$_2$ (AF)
1457 m	1454 sh	scis. CH$_2$		
1443 s	1440 sh	δ CH$_2$	1444 s	def. NH (GF)
1410 m	1410 m	ν_s COO$^-$	1412 w	ν COO$^-$
1392 w	1389 sh	ω CH$_2$		
1358 m	1358 m	τ CH$_2$	1355 w	def. CH$_2$ (AF)
1327 mw	1327 ms	ω CH$_2$	1325 m	def. CH$_2$ (AF)
1316 m		Δ CH$_2$		
1309 m		δ CH$_2$		
1287 w	1288 w	δ CH$_2$		
1268 w	1267 w	δ CH$_2$		
1218 w	1215 w	ω CH$_2$		
1176 mw	1177 w	ρ NH$_3^+$, ρ NH$_2$	1171 w	def. NH (TF)
1135 w	1134 w	ρ NH$_2$		
1085 m	1096 w	ν_s C–N	1088 s	def. NH (GF)
1069 ms	1049 wm	ν_s C–N		
1046 s		ω NH$_3^+$		
1020 mw	1022 w	ω CH$_2$		
997 mw	995 w	ρ CH$_2$	993 vw	def. CH$_2$ (AF)
971 s	968 w	ρ CH$_2$	978 w	def. CH$_2$ (AF)
899 w	897 w	sk ν C–C	934 m	def. CH$_2$ (AF)
	881 w	sk ν C–C	891 vw	def. CH$_2$ (AF)
858 w		ν C–C, τ NH		
848 wm	849 w	ω NH	839 m	def. NH (GF)
793 w	793 w	ρ NH$_2$	781 w	def. NH (GF)
759 w		δ COO$^-$		
746 w	746 w	ρ CH$_2$		
	702 mw	ρ CH$_2$		
675 w		ω COO$^-$	665 w	def. COO$^-$
613 w		ip δ O–C=O	611 w	def. COO$^-$
571 w	573 mw	ρ COO$^-$, τ NH$_2$	535 ms mult.	def. COO$^-$
524 m	525 m	τ NH$_3^+$, τ NH$_2$		
455 w	455 w	In phase δ C–C–C		
389 m		Out phase δ C–C–C		

[a] *Abbreviations*. TF: amino acid terminal fragment; GF: guanidinium fragment; AF: aliphatic fragment.

mines the orientation of the amino acid to the surface. The spectral observed behaviour and the proposed orientation is consistent with SERS selection rules [33]. This proposition also agrees with the results of DiCostanzo et al. [11] who described the stereochemistry of the guanidine–metal interactions in small molecules and proteins.

Additionally, the SERS spectrum in Fig. 3 displays several bands associated to different vibrations of the guanidinium group at about 1440, 1080 and 850 cm^{-1}. This suggests that the amino acid–metal surface interaction in solution is also verified through the guanidinium group as already proposed by considering the information obtained from the net charge value. Also it is possible to argue, because of the medium strong relative intensity of the bands at 1655 and 1565 cm^{-1}, that the α-amino and α-carboxylic groups interact with the Ag nanoparticles. This particular interaction is rather feeble in the case of the arginine coated by the metal, as it is possible to infer from the weak intensity of the corresponding bands in Fig. 4.

In general, the slight spectral differences mainly in frequencies between de Raman and SERS spectra could be related to electrostatic interactions as predicted by our theoretical calculations.

4.4. Theoretical aspects

Arginine was modelled with a positive net charge +1. This charge is mainly centred in the guanidinium fragment. Charged molecules tend to interact through long-range electrostatic forces. If so, then arginine will interact with the Ag layer in such a way to maximize such interactions.

In the case of the isolated silver bilayer, the HOMO and LUMO have the same energy (-6.14 eV) and the valence (the first valence band extends from -6.14 to -8.4 eV) and conduction bands overlap, indicating that the present microscopic model is a good representation of a metallic cluster. In a molecular orbital representation the HOMO, which is of π character, is located on almost all Ag atoms but not in the centre of the Ag surface.

In the final Arg–Ag geometry (see Fig. 5), the two terminal N atoms of the guanidinium group are at 3.2–3.4 Å from the closest Ag atoms. The arginine amino acid is placed perpendicularly to the area of the Ag surface in which the electronic density of the HOMO is zero. This is a suitable position for a guanidinium group which has an overall positive charge but with two N atoms carrying negative charges because it minimizes the electron–electron repulsion. Charge transfer is ruled out because the empty π MOs of arginine do not overlap with the HOMO of the Ag layer. Therefore, we may conclude that electrostatic interactions are the main factor of the arginine–Ag layer interaction.

5. Conclusions

The net charge value of arginine at pH close to 7 is an argument to infer about the SERS activity in colloidal solution. The H$_2$B$^+$ species is confirmed to display SERS activity besides its high hydrophilicity. A net SERS spectrum was observed for the amino acid coated

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by nanostructured Ag; this also allows to obtain a unique and reproducible spectrum. The SERS spectrum is dominated by signals coming from the guanidinium group, suggesting that the amino acid interacts with the metal surface, through that group. Particular vibrations of the aliphatic moiety suggest that the chain is perpendicular to the surface. Other fragments as the amino and carboxylic are also expressed but through weak spectral signals; these bands become intense in colloidal solution suggesting a different interaction in relation to the analyte coated by the metal. Theoretical calculations performed by using extended Hückel theory and 6-31G* methods for a model of interacting with an Ag cluster support the observed SERS results. Calculations confirm the inductive effect imposed by the guanidinium moiety of arginine orientates the molecule onto the surface. A preferred orientation or organization drove by arginine in a peptide was recently verified in our research group [34].

Acknowledgements

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