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SERS spectra of polyaniline thin films deposited on rough Ag, Au and Cu. Polymer film thickness and roughness parameter dependence of SERS spectra

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Abstract

Surface-enhanced Raman scattering (SERS) has lately proved to be an effective technique which has led to its increasing application for studying the structural properties of conducting polymer thin films. It is generally accepted that the enhancement process has an electromagnetic origin arising from the excitation of surface plasmons (SPs) in the metal support on which the polymer film is deposited. However, the electromagnetic enhancement is also accompanied by a chemical process, on which only scarce experimental data are available at present. The chemical process originates in an increased polarizability of the molecules at the metal surface under the action of an incident radiation, as a result of which new chemical bonds are formed with the atoms of the metal support. This paper is devoted to the study of the SERS spectra under 1064 nm excitation for two forms of polyaniline, one of the emeraldine base type and the other of the emeraldine salt type. Our purpose has been to identify the chemical effects at the polymer/metal interface that are involved in specific modifications of the SERS spectra. The following results concerning SERS spectrum variation with metal support type (Ag, Au and Cu) have been obtained. An oxidation of emeraldine base taking place at the polymer/metal interface has been revealed. In the case of emeraldine salt, an oxidized form of polyaniline, the SERS spectra remain unchanged regardless of the changes in the metal support, which proves the stability of this form. A new result has been obtained as SERS spectroscopy revealed an electron delocalization process taking place in the emeraldine salt molecule as a result of an electron transfer from metal to the polymer molecule occurring on the level of quinoid rings. The concept of a rough Raman-active surface has been clarified by using a parameter *h/a*, similar to the grating groove depth/grating periodicity ratio which occurs when a diffraction grating is used as optic coupler.

Keywords: Polyaniline; Surface-enhanced Raman scattering; Roughness

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1. Introduction

The study of conjugated-bond compounds has lately given particular attention to polymer conductors owing to their high potential for technological applications. The electrical conduction of polymers depends on the stereoregularity of their skeleton, which in turn depends on the position of carbon atoms to which radicals can attach during polymerization. Consequently, the investigation of their vibrational properties, which depend on their structure and doping state, is of particular interest. To better understand these properties, optical methods such as infrared spectroscopy and Raman spectroscopy are widely used. In both fundamental research and a broad range of applications, conducting polymers are used in the form of thin films, for which specific experimental techniques have to be adapted and developed.

Within this framework, the surface-enhanced Raman scattering (SERS) has lately proved to be a very useful technique for providing high-quality spectra, which make it possible to observe the structural details of polymer films even at very low surface coverage [1–3]. Even though many details of the process have yet to be understood, it is generally admitted that exaltation has a double origin: an electromagnetic one and a chemical one [3]. The electromagnetic origin of exaltation, which seems to predominate in SERS, involves an excitation of surface plasmons (SPs) confined to three metals: Ag, Au and Cu. Unlocalized SPs, also known as propa-

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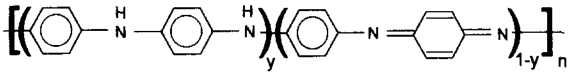
gating SPs, can undergo resonant excitation under the influence of light when the component parallel to the interface of the light radiation wave vector is equal to the real component of the SP wave vector [4]. To do this in practice, one may use either a prism [5–8] or a diffraction grating [9,10] as optical couplers. An intense electromagnetic field arising at the interface of the metal and ambient medium excite Raman transitions in the molecules that are adsorbed on the metal surface in contact with the environment. Part of the Raman radiation in turn excites the SPs at Stokes frequency, which is afterward decoupled as propagating Raman radiation inside the prism [8], or emerges as a diffracted radiation along a well-defined direction depending on the grating periodicity when the coupler is a diffraction grating. But using prisms or gratings as optical couplers is rather cumbersome in SERS spectroscopy. Therefore, SERS studies mostly use metallic supports Ag, Au or Cu as a rule with a roughness-type microstructure in the 10 to 100 nm range. In this case, the electromagnetic exaltation of Raman scattering occurs through an excitation of the SPs that are located across metal support roughness. Metal surface morphology acquires a special relevance in this case. From a purely qualitative perspective, the rough metal support may be regarded as a sum of diffraction gratings with different grating periodicity, shorter than the excitation radiation wavelength.

The chemical origin contribution to the SERS process is harder to identify or assess in quantitative terms. The chemical mechanism contributing to Raman scattering exaltations is based on an increased polarizability of the molecules that are adsorbed on the metal surface under the influence of incident radiation, as a result of which new chemical bonds with the metal surface are formed. In this case polarizability becomes much higher than that of free molecules [11]. When electronic transitions are involved and only certain bands associated with entirely symmetrical vibrations are exalted, this process can be considered similar to resonant Raman scattering. The chemical mechanism is usually accompanied by a metal–molecule or molecule–metal charge transfer, which partly accounts for the success of SERS studies using materials with empty π^* orbitals. This leads to the conclusion that the chemical contribution to SERS spectra depends in intensity on the physical and chemical properties of the metal support and of the polymer deposited on it. The way that polymer thin films are prepared is yet another cause for SERS spectrum disturbances. When thin films are prepared from polymer solution by evaporation of the solvent, or by deposition on metallic electrodes through cyclic voltammetry as is the case for in situ studies, the SERS spectra are often modified by an interfacial reaction across the metal support, i.e. polymer deposition may be preceded by electrode oxidation [12–15].

This paper is devoted to SERS studies carried out for polyaniline thin layers deposited on rough metallic films. The purpose is to identify interfacial chemical reactions across the metal support leading to a variation of SERS spectra depending on the metal support: Ag, Au and Cu. The results were obtained by scanning electron microscopy observation of metal supports with similar roughness. Experimental data on SERS spectrum variation with metal support type, particularly the position and relative intensity of certain Raman lines, show that such variation is observed for the Raman lines associated with vibrations involving those atoms of the polymer molecule and those bonds that can chemically interact with the metal support, which involves interfacial chemical effects. A new result has been obtained concerning the different variation with polymer film thickness of the SERS spectra for emeraldine base and emeraldine salt, respectively. This is accounted for by the contribution of two effects: a chemical effect at the polymer/metal support interface, and an electromagnetic effect via the SPs.

2. Experimental

It is well known that the polyaniline repeating units can contain two different entities: a reduced state, leucoemeraldine, $y=1$; and an oxidized state, pernigraniline, $y=0$.



An intermediate state, in which the oxidation and reduction degrees of polyaniline are equal to each other, $y=0.5$, corresponds to a state known as emeraldine. The emeraldine in its turn can be considered to have two basic structures. In this paper, we used an emeraldine in the form of powder with two basic structures — one of emeraldine base and the other of emeraldine salt type — obtained by chemical polymerization. For comparison the SERS spectra for emeraldine salt deposited on Ag and Au electrodes by cyclic voltammetry were also studied.

The polymer thin films were deposited on rough Ag, Au and Cu supports by evaporating the solvent in a nitrogen atmosphere from a volume of 0.1 cm^3 of solution uniformly distributed on each square centimeter of every sample. SERS spectra were recorded no more than 1 h after the sample preparation. The polymer solutions were prepared in two solvents, namely, chloroform ($CHCl_3$) and *N*-methyl-2 pyrrolidinone (C_5H_9NO), abbreviated NMP. The average thickness of the polymer film deposited on the metallic surface of each sample was determined from the known values of polymer solution concentration and polymer density.

The strong dependence of SERS spectrum intensity on metal support roughness [4,5] imposes certain restrictions on the technique of preparation of the metal films. We used the vacuum evaporation technique with a deposition rate of 1 nm/s at a pressure lower than 10^{-5} Torr, with the atomic beam at almost grazing incidence ($\theta_{in} \approx 80°$) on the microscope slide used as a target support [16]. The decrease in the incidence angle θ_{in} of the atomic beam modifies the roughness

Fig. 1. Scanning micrograph of rough Au support with high SERS activity.

of the metallic film which in turn determines an important decrease of the intensity of the SERS spectra. By controlling the evaporation geometry and the quantity of evaporated metal, we ensured a good reproducibility of the thickness and roughness of the metal films used as supports in our SERS experiments. This led to variations smaller than 15% in the Raman intensities observed with polymer films of the same thickness deposited on the same metal support type, which is quite satisfactory for this kind of measurement.

The Raman-active metallic films prepared by means of the above technique were inspected by scanning electron microscopy. A typical aspect of a rough gold surface with a good Raman activity is presented in Fig. 1. To avoid the disturbing photoluminescence background appearing when a visible excitation is used, the SERS studies reported in this paper were carried out under 1064 nm laser excitation. The spectra were recorded in a back-scattering geometry with an FT Raman Bruker RFS 100 analyzer spectrometer.

3. Results and discussion

3.1. Variation of the SERS spectra with the type of metallic support and with polymer film thickness

SERS spectra that were recorded on thin films deposited on Ag, Au and Cu metal supports for chemically prepared emeraldine base and emeraldine salt are shown in Fig. 2(a) and (b), respectively. For the sake of comparison, we used metal supports of similar roughness as determined by scanning microscopy. For further comparison, the SERS spectra of emeraldine salt obtained by cyclic voltammetry on Ag and Au electrodes are given in Fig. 2(c). Tables 1 and 2, which were derived from Fig. 2, show the positions of the Raman lines, observed by in situ measurements, and the vibrations associated with them [17,18], as well as the positions of the Raman lines observed in this paper by ex situ SERS measurements. Our experiments have proved that the results in Fig. 2(a), (b) stay virtually unchanged regardless of the solvent, chloroform or NMP, that had been used to prepare

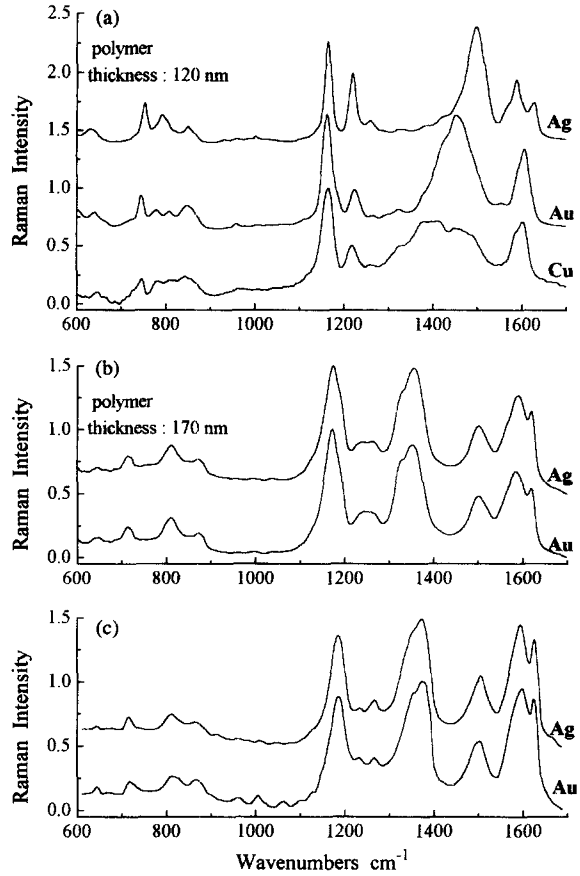


Fig. 2. SERS spectra of polyaniline films: (a) emeraldine base and (b) emeraldine salt structures prepared by chemical polymerization deposited on rough Ag, Au and Cu supports; (c) SERS spectra of emeraldine salt films prepared on Ag and Au electrodes by cyclic voltammetry.

Table 1
Vibration modes observed by SERS spectroscopy in emeraldine base (cm^{-1})

Emeraldine base				Assignments [17]
647.1 nm Raman spectra In situ Exp. [17]	1064 nm SERS spectra Exp. [this work]			
	Ag	Au	Cu	
1618	1624			C–C stretch. (B)
		1605	1602	
1586	1585		1586	C=C stretch. (Q)
1553			1483	C–C stretch.
1480		1455	1455	C=N stretch.
1420		1424	1412	C–C stretch.(Q)
	1258	1264	1263	C–H bending (B)
1217	1217	1223	1220	C–N stretch.
1160	1162	1160	1162	C–H bending (Q)
	930	958	963	ring deformation
870	849	848	843	ring deformation
826		804	803	amine deformation
788	791	780	778	ring deformation (Q)
750	748	745	744	imine deformation
640	632	638	645	ring deformation

Table 2
Vibration modes observed by SERS spectroscopy in emeraldine salt and semiquinoide-radical structure (cm^{-1})

Semiquinoide structure			Emeraldine salt			Assignments [18]
1064 nm In situ [18]		647.1 nm In situ [18]	1064 nm SERS [this work]			
Exp.	Calc.	Exp.	Chemical polymerization		Cyclic voltammetry	
			Ag	Au	Ag/Au	
			1621	1620	1626	C–C stretch. (B)
	1614	1612				+ C–H bending (B)
1590	1591	1593			1594	C–C stretch. (B) + C=C stretch.
	1581	1579	1589	1587		C=C stretch. (Q) + C–C stretch.
1507	1496	1480	1501	1501	1506	C=N stretch.
	1417	1418				C–C stretch. (Q) + C–H bending (Q)
1350–1330				1380–1330		protonated structure
1260	1265		1266	1266	1268	C–H bending (B)
	1207	1215	1234	1238	1236	C–N stretch. + C–C stretch. + C–H bending (B)
1170	1171		1173	1174	1181	C–H bending (B)
	1155	1157				C–H bending (Q)
	880		873	873	871	ring deformation (B)
810	800	788	811	810	812	ring deformation (Q)
714	704	749	715	714	716	inter-ring deformation
	612		648	645	646	ring deformation (Q)

the polymer solutions from which the polymer films were obtained.

Two major facts derive from the results in Fig. 2:

(i) In the case of polymer films ranging from 100 to 200 nm in thickness, the SERS spectra of emeraldine base are seen to depend on the type of metal support.

(ii) In the case of emeraldine salt, aside from the variation of the overall scattered intensity variation, the Raman spectra do not vary with either metal support or polymer preparation technique, whether chemical or electrochemical.

Accounting for these results is an extremely hard task. It should be pointed out for a start that the variations found in the Raman spectra originate from the overlapping of two processes that are involved in SERS generation: (a) a process of electromagnetic origin, via the excitation of SPs located on the rough surface, which may account for the variation of the overall intensity of the SERS spectra with the type of metal support (due to a variation of the metal's dielectric constant with the excitation wavelength), its roughness characteristics, and polymer film thickness; all of these finally result in how the polymer film is 'seen' by the evanescent wave; (b) a more subtle, harder to understand chemical effect, which yet can be construed as a redox process that may occur between the polymer film and the metallic support. Since such a process is a priori dependent on the oxidizing nature of the metal support, its importance in the generation mechanism of the SERS spectrum should increase as polymer films decrease in thickness.

As expected, the SERS spectra of emeraldine base and emeraldine salt, which differ in oxidation degree, are different from each other. In addition, Fig. 2 shows a new result, namely, that the SERS spectra of emeraldine base also depend on metal support type. The variation of the SERS spectra with metal support type actually concerns two distinct aspects: the overall scattered intensity variation, and the position and relative intensity variations of certain Raman lines, particularly those associated with vibrations involving conjugated bonds. As far as the overall scattered intensity or, in other words, the SERS mechanism efficiency is concerned, we find that, keeping the same roughness for different metal supports and the same polymer film thickness, the Raman intensity is decreased by a factor of two or five as we change from Au to Ag, and Cu, respectively. The result may be associated with an electromagnetic excitation origin of the SERS spectra, via the SPs.

The second type of SERS spectrum variation with metal support type is only found in emeraldine base (Fig. 2(a)). This variation is a consequence of the oxidizing properties of the metal supports. As mentioned above, emeraldine base is a form of polyaniline in which two different structures coexist: a reduced structure (Form A) and an oxidized structure (Form B). The coexistence of these two forms occurs as a consequence of the reversible nature of the shift from Form A to Form B, as in a redox system.

A redox system has an associated redox potential. The reversibility of the A ↔ B process is disturbed by the presence of a metal. The loss of electrons by the metal enhances the reduction reaction. Consequently, the redox equilibrium shifts to favor the generation of Form A. Transition from Form A to Form B occurs at a potential that reflects the electron affinity of Form B, thus defining the oxidizing nature of the metal. Hence, the reduction process will depend on the type of metal, more specifically on its first ionization potential. Consequently, at the metal/polymer interface, the metal can switch to an ionized state by releasing an electron:

$$\mathrm{Ag}-1e^{-}\rightarrow\mathrm{Ag}^{+}\quad[\mathrm{Kr}]4\mathrm{d}^{10}5\mathrm{s}^{1}\rightarrow[\mathrm{Kr}]4\mathrm{d}^{10}$$

$$\mathrm{Au}-1e\rightarrow\mathrm{Au}^{+}\quad[\mathrm{Xe}]4\mathrm{f}^{14}5\mathrm{d}^{10}6\mathrm{s}^{1}\rightarrow[\mathrm{Xe}]4\mathrm{f}^{14}5\mathrm{d}^{10}$$

$$\text{Form B}+2\mathrm{H}^{+}+2e^{-}\leftrightarrow\text{Form A}$$

The difference in first ionization potential accounts for the different behavior of these metals. Comparing Ag with Au, we have $7.57<9.22$ eV. Consequently, Ag will favor the reaction from right to left. As a result, more benzenoid rings than quinoid rings will be adsorbed on the Ag surface. In the case of Au, the reaction proceeds the other way around, namely, from left to right. As a result, equilibrium will be tipped in favor of the quinoid rings, which will be prevailingly adsorbed across the metal surface. This reasoning will be proved valid if two types of experimental results are obtained, namely:

(i) For the emeraldine salt in oxidized form, the SERS spectra, measured on relatively thick films of 100–200 nm, do not depend on the metal support type. This is clearly illustrated in Fig. 2(b) and (c) where the spectrum of emeraldine salt remains unchanged no matter whether Ag or Au is used, and regardless of how the emeraldine salt has been prepared, i.e. by chemical synthesis or cyclic voltammetry.

(ii) For emeraldine base, specific variations are observed between the relative intensities associated with the two structures, quinoid and benzenoid rings, respectively. Let us now look at the data in Fig. 2(a), particularly at the relative intensities of the bands which have their peaks at about 1624 and 1582 cm^{-1}, associated with C–C stretching deformation in benzenoid rings and with –C=C– stretching in the quinoid rings, respectively. The above reasoning is seen to be experimentally confirmed as the Ag and Au supports give rise to specific changes in the relative intensities of these bands.

The effect of emeraldine base turning more strongly oxidized or reduced depending on the metal support should be even more evident if measurements are made on thinner polymer films (about 10–50 nm) where the interfacial chemical effect caused by the metal support gets an increased importance in the SERS mechanisms. Fig. 3 shows the results obtained on emeraldine base films of about 30 nm in thickness. Curve 4 on the same figure presents the SERS spectrum of an 85 nm film of emeraldine salt deposited on Ag. In Fig. 3, the results illustrate a gradual transformation of the SERS spectra of emeraldine base as different metals, Ag, Au and Cu, respectively, are used as supports. The change observed in emeraldine base consists in its spectrum growing more like that of emeraldine salt. Right now, it is hard to understand why Cu should appear to cause the strongest oxidizing effect, even though its first ionization potential of 7.72 eV is rather close to that of Ag.

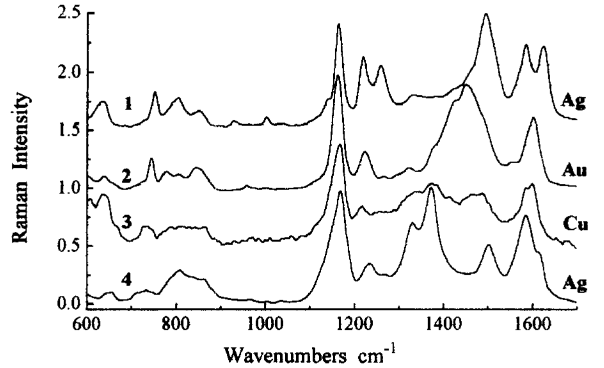


Fig. 3. SERS spectra of emeraldine base films of 30 nm thickness deposited on (1) Ag, (2) Au and (3) Cu; (4) corresponds to the SERS spectrum of 85 nm emeraldine salt film.

Let us now take a look at how SERS spectra vary not just with metal support type, but also with polymer film thickness. This will provide a more detailed understanding of the chemical effect occurring at the metal/polymer interface. The results illustrating the variation with polymer film thickness of the SERS spectra of emeraldine base and emeraldine salt are shown in Figs. 4 and 5.

The variations found in the SERS spectra refer to two different aspects: the variation of the overall intensity of Raman radiation, and a change affecting the positions and especially the relative intensities of certain Raman spectrum lines.

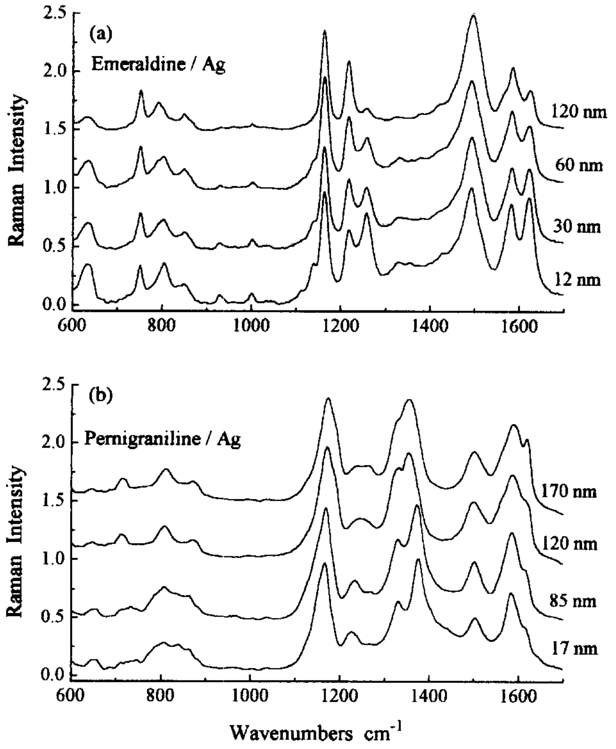


Fig. 4. Thickness dependence of SERS spectra of (a) emeraldine base and (b) emeraldine salt deposited on rough Ag supports.

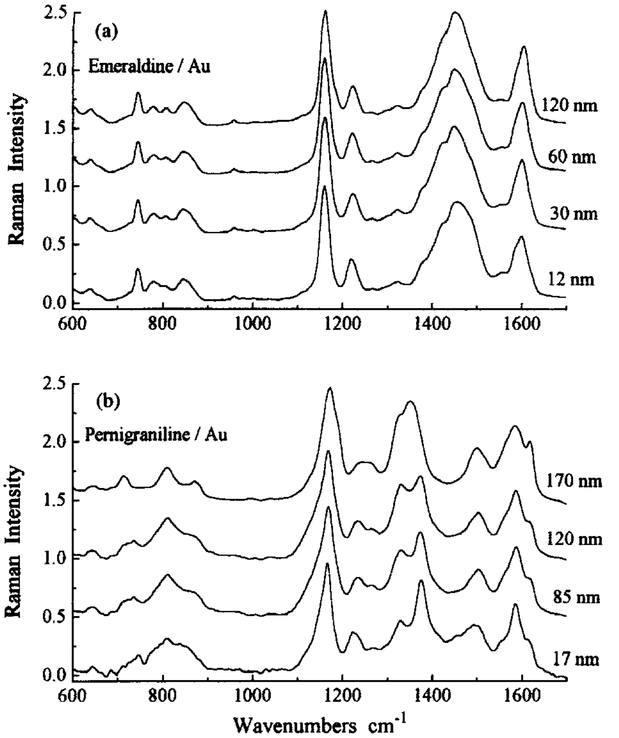


Fig. 5. Thickness dependence of SERS spectra of (a) emeraldine base and (b) emeraldine salt deposited on rough Au supports.

As far as the former is concerned, the overall intensity variation is found to behave differently depending on film thickness range. In the high thickness range of 200 to 50 nm, the overall scattered intensity for both emeraldine types decreases in virtually direct proportion with the decrease in polymer film thickness. In the lower range of 50–10 nm, the overall intensity decrease is no longer linear but rather asymptotically tends toward a value which is clearly dependent on the type and roughness characteristics of the metal support.

Changes in the positions and especially the relative intensities of some Raman spectrum bands depend on both the type of polymer investigated and metal support type. SERS spectrum variation with film thickness is found to differ for emeraldine base and emeraldine salt, respectively, with a stronger influence occurring in the Raman lines related to the vibrations that are associated with quinoid and benzenoid rings. In the case of emeraldine base, the relative intensities of the Raman lines are found to vary with polymer film thickness only when Ag is used as metal support. A completely different variation is seen in emeraldine salt. Emeraldine salt films of equal thickness exhibit no change in the Raman spectra, no matter whether Ag or Au is used as metal support. However, when polymer film thickness is reduced, some changes do occur in emeraldine salt as well, but they remain the same whether Ag or Au is used, thus showing no dependence on metal support type.

Accounting for these results is harder than for the previous set. Let us now examine the spectra in Figs. 4 and 5. Firstly, it is observed that, for emeraldine base, the SERS spectra vary with polymer film thickness only when Ag is used as metal support. Secondly, this intricate mechanism of Raman spectrum variation with polymer film thickness mostly affects certain bands: about 1624 cm^{-1}, associated with C–C stretching deformation in benzenoid rings; about 1582 cm^{-1}, corresponding to –C=C– stretching in the quinoid rings; about 1257 cm^{-1} C–H, corresponding to a bending in benzenoid rings; and about 1217 cm^{-1}, which corresponds to C–N stretching deformation. Moreover, Fig. 4(a) shows that, for Ag, we only have a relative intensity variation in the bands at 1624 and 1257 cm^{-1}, both associated with benzenoid rings. In this case, too, one can account for it based on the different oxidizing properties of Ag and Au. Consequently, in the case of the emeraldine base/Au system where SERS spectra do not change with polymer film thickness (Fig. 5(a)), one can assume that there is no interfacial chemical effect. By contrast, such an interfacial effect is evident in the emeraldine base/Ag system. A detailed understanding of this effect is not an easy task for the time being.

An invariance of the SERS spectra with metal support type, Ag or Au (Fig. 2(b), (c)), for emeraldine salt films in the high thickness range (120 to 170 nm), leads to the conclusion that emeraldine salt has a more stable molecular configuration, less reactive with the metal support. Unfortunately, this deduction is not entirely accurate since it disagrees with the results in Figs. 4(b) and 5(b), which show that emeraldine salt itself undergoes SERS spectrum variation for lower thickness values of the polymer films. In the case of emeraldine salt, unlike that of emeraldine base, spectrum variation with polymer film thickness no longer depends on metal support type. Keeping the same thickness of the emeraldine salt films, we find that the spectra are virtually identical no matter whether the metal support is Ag or Au. In this case, too, SERS spectrum variation with polymer film thickness consists of relative intensity variations in the bands at about 1624 and 1582 cm^{-1}. In addition, the SERS spectrum of emeraldine salt contains a broad band in the range 1320–1380 cm^{-1}, which is formed by an overlapping of two bands with peaks at about 1328 and 1365 cm^{-1}. This double band was also observed by in situ measurements, where it appeared within the potentials of the first redox process and was associated with the oxidized form of polyaniline. This band has been attributed to semiquinone radical structures, more precisely to C–H bending in quinoid rings (about 1328 cm^{-1}) and C–C stretching in quinoid rings, plus C–H bending in benzenoid rings (about 1365 cm^{-1}) [17,18]. The coexistence of two bands of different intensities indicates that inside of the distribution of semiquinone radical structures could exist different configurations [17]. In our case, when polymer film thickness is decreased, the band at about 1365 cm^{-1} grows in intensity at the expense of the 1328 cm^{-1} band. This suggests that such distribution of semiquinone radical structures is not uniform across the polymers layers either, which, in our view, could be a consequence of their proximity to the metal support, i.e. of an electron transfer from the metal to the polymer molecule. This electron transfer occurs on the level of quinoid rings, leading to a delocalization of the electrons similar to the one occurring in the benzenoid rings. The process has to be accompanied by specific changes in the Raman bands at about 1328 and 1365 cm^{-1}, i.e. a relative exaltation of the band at about 1365 cm^{-1} associated with the benzenoid ring, which is confirmed by the experiments.

It must be mentioned that this delocalization of the electrons out of the molecular chain is caused by their proximity to the Ag or Au metal support, which accounts for the SERS spectrum variations with polymer film thickness. Such delocalization, which can easily be noticed on films in the 10 to 50 nm thickness range, is independent of metal support type and should not be attributed to an interfacial chemical effect consisting in a transition of emeraldine from its protonated form to reduced form. As a matter of fact, the latter assertion appears to be confirmed by the variations of the bands at about 1624 and 1582 cm^{-1}. Figs. 4(b) and 5(b) show that the band at about 1582 cm^{-1} grows in intensity at the expense of the 1624 cm^{-1} band, which indicates the persistence of the quinoid structure as a prevailing specific form of emeraldine salt. Given our current state of knowledge, we are inclined to regard the latter results as the consequence of an interaction between the evanescent waves and the polymer film, with the penetration depth of the evanescent waves into the polymer film eventually leading to the SERS spectrum variation with polymer film thickness.

3.2. Variation of the SERS spectrum intensities with roughness parameters

At this point, we have to indicate what we mean by roughness and its characteristics from the perspective of SERS. Scanning microscopy images of rough SERS-active surfaces of Ag and Au were presented in an earlier paper [15]. In Fig. 1 is shown a SERS-active surface of Au. In qualitative terms, such rough surfaces may be likened to a bird's-eye view of a multitude of columns of nearly the same diameter and at a certain tilt from the vertical. Based on this image, we may describe surface roughness in terms of two quantities: *a* and *h*, the diameter and average height of these columns, respectively. In the case of rough SERS-active surfaces, the tilt of the columns is due to our preparation technique, as the metal was deposited on the glass support at almost grazing incidence [16].

We described in an earlier paper [19] some peculiarities of the SERS emission when a diffraction grating was used as optical coupler. We showed at the time that, in the circumstances of an excitation of SPs, the SERS intensity depends on the ratio between grating groove depth and grating periodicity. We also proved experimentally that there was an optimum groove depth of the grating for which Raman efficiency was highest.

By idealizing the Ag, Au and Cu surfaces used in this paper, we may assimilate the rough surfaces with two-dimensional diffraction gratings. In this case, the roughness ratio, *h/a*, may be likened to a grating groove depth/grating periodicity ratio. If this is correct, any change in the *h/a* value should be illustrated by a specific variation of the SERS intensity. Such a variation is shown in Fig. 6, which presents results concerning two polymers, poly(3-alkylthiophene) and emeraldine base, deposited in thin films on rough Au supports. We preferred to use Au rather than Ag because the chemical reactivity of the former is lower than the latter. Operating on the film preparation techniques, we managed to obtain films of different, controlled roughness values; more specifically we obtained a variation of *h* in the *h/a* ratio. The results in Fig. 6 were assessed by scanning microscopy; it was found that, keeping the same deposition geometry and changing metal film thickness, the parameter *h* was changed too. Fig. 6(a) illustrates an idealized change in metal support roughness by means of different preparation techniques. This roughness change was observed by scanning microscopy. To obtain it, we used controlled evaporation conditions, namely, we kept the atomic beam at a constant incidence angle to the target surface and changed the amount of evaporated metal in a controlled manner. We thus varied the thickness, *e*, of the metallic film and the parameter *h* in the *h/a* ratio, which are both involved in a SERS signal optimization. The results

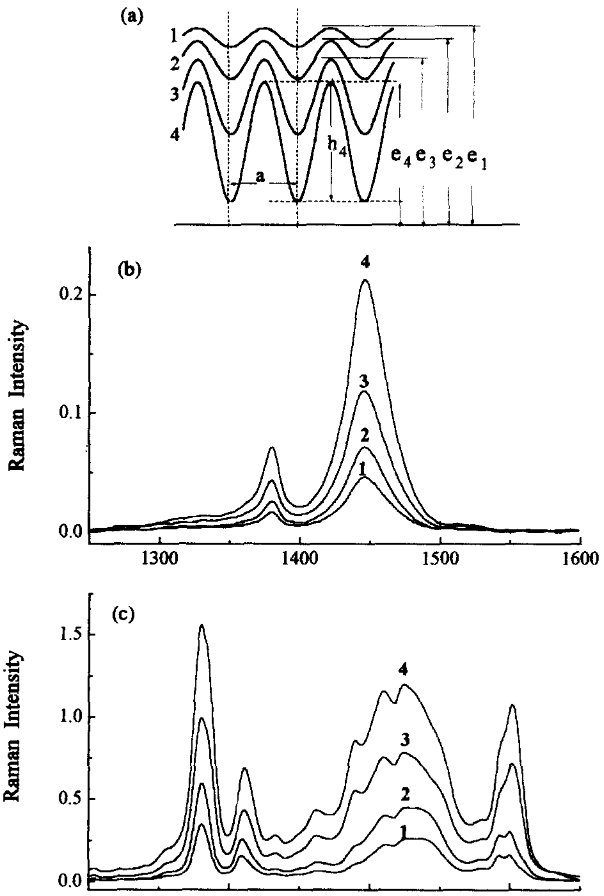


Fig. 6. (a) Idealized change in the metal support roughness by means of different preparation techniques; roughness dependence of SERS intensities of (b) poly(3-hexylthiophene) and (c) polyaniline-emeraldine base structure. Spectra (1)–(4) from (b) and (c) correspond to the (1)–(4) roughness profiles in (a).

Table 3
Variation of the SERS intensity as a function of metallic film thickness and roughness parameter

Au film thickness *e* (nm)	Parameter *h* (nm)	Raman intensity (normalized scale) Calc.	Raman intensity Poly(3-hexylthiophene) Exp.	Raman intensity Emeraldine Exp.
250	12	1	1	1
150	20	1.67	1.7	1.72
100	35	2.9	3.0	2.9
60	50	4.1	5.1	4.5

shown in Fig. 6 are summarized in Table 3 where experimental data and calculation-predicted data are compared in terms of the relative variation of *e* and *h/a*. The calculated Raman intensity variation is found to be in very good agreement with the experimentally measured variation.

4. Conclusions

The surface-enhanced Raman scattering (SERS), a most useful technique for thin film investigation, has lately been increasingly applied to the study of conducting polymers. Some details of the exaltation process have yet to be elucidated. It is, however, widely accepted that the exaltation of the surface Raman scattering stems from a double origin: electromagnetic and chemical. The chemical contribution to the exaltation process remains a controversial issue. It depends on the chemical interactions at the metal/dielectric interface, which in turn depend on the types of metal and dielectric that are in contact. Hence a first conclusion: namely, the identification of an interfacial chemical process is no longer of the same generality degree as the one implied by the electromagnetic exaltation mechanism.

SERS spectra excited at 1064 nm for two forms of polyaniline, one of emeraldine base type and the other of emeraldine salt type, were studied in this paper. Our goal was to identify the chemical effects at the polymer/metal interface that are involved in specific SERS spectrum modifications.

The following results have been obtained:

(i) SERS spectra of emeraldine base were shown to depend on the type of metal support, namely, Ag, Au or Cu. This dependence stems from a double origin: an electromagnetic origin, via the SPs which are associated as the Raman scattered intensity changes with metal support type; and a chemical one, revealing an oxidation of emeraldine base, which is located at the polymer/metal interface.

(ii) The SERS spectra of emeraldine salt remain unchanged when the metal support is changed, which proves the stability of this protonated form.

(iii) SERS spectrum variation with polymer film thickness has revealed an electron delocalization taking place in the emeraldine salt molecule, as a result of an electron transfer from metal to the polymer molecule on the level of the quinoid ring.

The paper, in the authors' view, provides a more precise account of the concept of a rough Raman-active surface. This has been achieved by using an *h/a* parameter similar to the grating groove depth/grating periodicity ratio occurring when a diffraction grating is used as optic coupler.

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