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Structural properties of some conducting polymers and carbon nanotubes investigated by SERS spectroscopy

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Abstract

In this paper, we present Surface Enhanced Raman Scattering (SERS) experiments performed successfully on some conducting polymers and carbon nanotubes deposited in thin films on rough metallic surfaces. The enhancement mechanism in SERS has a twofold origin: electromagnetic and chemical. The electromagnetic enhancement is, however, the dominant mechanism and consists in the excitation of localized and delocalized surface plasmons (SP). The second enhancing mechanism for SERS, not yet convincingly supported by experimental data, is of chemical origin. This mechanism is due to the increase of the polarizability of the molecules on the metal surface under the action of the incident radiation, leading to the formation of new chemical bonds between the molecules and the metal surface. Unfortunately, the experimental data available to argue the presence of a chemical process are scarce and scattered. In this paper, we try to present some details regarding this aspect. In order to do so, we studied poly 3-hexylthiophene (3-PHT) and polyaniline (PAN) as a function of the type of the rough metallic support (Ag, Au or Cu), the oxidization state and thickness of the polymer layer. We studied also carbon single walled nanotubes. Our experiments reveal the existence of a chemical surface effect. The results obtained for 3-PHT show that SERS spectra depend on the oxidizing properties of the metal surface and on the nature of the solvent. This dependence is explained by the existence of some interfacial reactions that lead to the formation of interface compounds. The SERS measurements reported here reveal an increase of the intensities of the Raman lines, accompanied by a modification of the corresponding intensity ratios, when the degree of doping is increased. We observe for the first time by SERS spectroscopy that doping of 3-PHT with $FeCl_3$ leads to the appearance of a state of disorder in the structure of the macromolecular chain, as a result of steric hindrance effects. The type of the rough metallic support can modify SERS spectra and such an effect is clearly shown for the polyaniline case. No such dependence on metallic support type is observed on the SERS spectra of carbon nanotubes.

Keywords: Raman scattering; Surface studies; Conducting polymers; Polyaniline; Polythiophene; Carbon nanotubes

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1. Introduction

The study of conjugated-bond compounds has lately given a 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 absorption and Raman spectroscopy are widely used. In both fundamental research and a broad range of applications, polymeric conductors 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 that provides high quality spectra and allows the observation of fine structural

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details of films with very small thickness [1–3]. Even though many details of the process have yet to be understood, it is generally admitted that the SERS exaltation has a double origin: an electromagnetic one and a chemical one [4]. The electromagnetic enhancement is however the dominant mechanism. This mechanism consists in the excitation of localized and delocalized surface plasmons (SP) and is effective in copper, silver and gold.

It is well known that the delocalized surface plasmons, also called propagating surface plasmons, may be produced by optical excitation when the component parallel to the interface of the electric wave vector of the incident light equals the real part of the wave-vector of the surface plasmons [5]. In practice, this condition is realized by means of an optical coupler, which can be a prism [6,7] or a diffraction grating [8]. The intense electromagnetic field that exists at the interface between the metal and the surrounding medium excites Raman transitions in the molecules adsorbed on the metal surface. Part of the Raman radiation thus produced excites in turn surface plasmons at the Stokes frequency, and then decouples as a propagating Raman radiation inside the prism [9] or emerges as a diffracted radiation along a well-defined direction depending on the grating periodicity when the coupler is a diffraction grating [10]. To do this in practice, i.e., using a prism or a grating as optical couplers, is rather cumbersome in SERS spectroscopy. If the metal support has a rough microstructure with dimensions in the range 10–100 nm, the enhancement mechanism is the same. As a result, such a technique is much more attractive. Qualitatively, the rough metallic support may be considered a ‘‘superposition of diffraction gratings with different periods, each period being smaller than the wavelength of the exciting radiation’’. In this case, the morphology of the metal surface becomes very important for SERS spectroscopy. The magnitude of the enhancement factor depends on the properties of the metal used (the dielectric constant and the state of the surface) and on the wavelength of the exciting radiation. The second enhancing mechanism for SERS, of chemical origin, 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 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. This mechanism is, as a rule, accompanied by a charge transfer metal–molecule or molecule–metal, which explains in part the success of the SERS studies on materials with empty π^* orbitals.

The way how polymer thin films are prepared is yet another cause for SERS spectrum disturbances. Three types of samples are customarily used: (i) thin films deposited directly on the rough metal (Ag or Au) support by vacuum evaporation or sublimation; (ii) thin films obtained by evaporating the solvent, in vacuum or a controlled atmosphere, from a polymer solution of known concentration uniformly distributed on the metal surface, (iii) thin films electrochemically deposited on metal electrodes by cyclic voltammetry. This last procedure is also used for in situ SERS studies. If the last two procedures are used, the SERS spectra are often influenced by the appearance of an interfacial reaction at the metal surface, because the deposition of the polymer film is preceded by the oxidation of the electrode [12–15]. The present work is a synthesis of our research on the SERS spectroscopy of conducting polymer thin films. Special attention has been given now to the dependence of the SERS spectra on: (i) the type of the metal support and its roughness characteristics, by analogy with the use of a diffraction grating as an optical coupler, (ii) the type and thickness of the polymer film, (iii) the appearance of interfacial chemical reactions between the metal and the solvent. For some polymers, in our case poly(3-hexyl thiophene) (3-PHT), the doping process by means of the Lewis acid ($FeCl_3$) generates the establishment of a state of disorder in the molecular chain, which is observed in the SERS spectra by the modification of the Lorentzian profile of the Raman lines. This modification consists in the appearance of a contribution of Gaussian type in the low energy wings of the Raman lines. The paper also reports for the first time results on the SERS spectroscopy of nanometric structures, particularly SERS spectra of carbon nanotubes.

2. Experimental

2.1. Roughness of the metal support

The polymer thin films were deposited on rough Ag, Au or Cu supports. The strong dependence of the SERS spectrum intensity on the metal support roughness [4,5] imposes certain restrictions on the 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 ($\theta_{in} = 80°$) on a microscope slide used as a target support [16]. The decrease of the incidence angle θ_{in} of the atomic beam modifies the roughness 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 approximate thickness deposited on the same metal support type, which is quite satisfactory for this kind of measurements. The Ra-

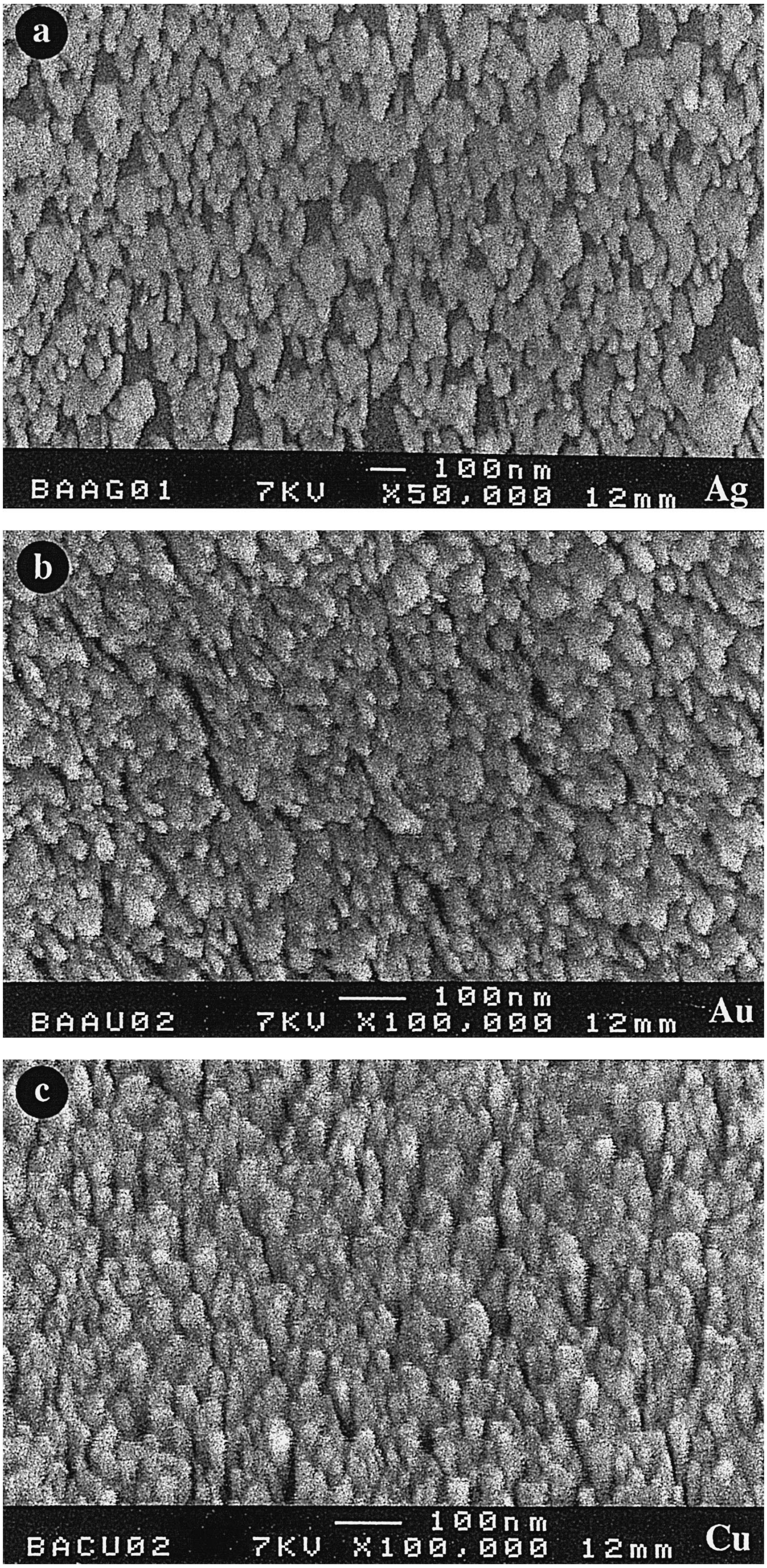
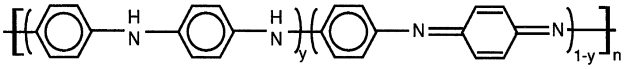


Fig. 1. Scanning microscopy pictures of rough silver (Ag), gold (Au) and copper (Cu) supports with high SERS activity.

man active metallic films prepared by means of the above technique were inspected by scanning electron microscopy. A typical aspect of a rough surface with a good raman activity is presented in Fig. 1.

2.2. Polymer samples

In this work, we used two polymers: polyaniline and poly(3-hexyl thiophene). The polymer thin films were deposited on rough metallic 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. 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. It is well known that the polyaniline repeating unit can contain two different entities: a reduced structure, leucoemeraldine with $y=1$ and an oxidized structure, pernigraniline with $y=0$. A schematic form of this polymer is presented below:



An intermediate structure, in which the oxidation and reduction degrees of the two units of polyaniline are equal to each other, $y=0.5$, corresponds to a structure known as emeraldine. To obtain a polyaniline in which one of these forms is predominant depends on how it is prepared. We used a polyaniline in the form of powder with two basic structures—one of emeraldine and another of pernigraniline type—obtained by chemical polymerization. SERS spectra of pernigraniline deposited on Ag and Au electrodes by cyclic voltammetry were also studied.

The 3-PHT regio-regular polymer has been obtained in the form of powder by chemical polymerization of the 3-hexyl thiophene monomer by means of the Lewis acid ($FeCl_3$) and by extracting the soluble fraction in dichloromethane (CH_2Cl_2) with an average gravimetric molecular weight Mn = 8370 g/mole.

2.3. Solvents

Above, we specified how the polymer layers were deposited on rough metallic supports by evaporating the solvent from polymer solutions of different concentration. For polyaniline including the two basic structures of different weight, one of emeraldine and the other of pernigraniline type, the polymer solutions were prepared in two solvents, namely chloroform ($CHCl_3$) and *N*-methyl-2 pyrrolidinone (C_5H_9NO) abbreviated NMP. For the poly(3-hexyl thiophene) solutions, we used two solvents: chloroform ($CHCl_3$) and tetrahydrofuran (C_4H_8O), abbreviated (THF), which have different reactivities with respect to the metal support, Ag or Au.

2.4. SERS measurements

To avoid the disturbing photoluminescence background appearing when a visible excitation is used, the SERS studies reported in this paper were carried out under the 1064 nm laser excitation. Spectra were recorded in a back scattering geometry with an FT Raman Bruker RFS 100 spectrometer.

3. Results and discussion

3.1. Variation of the SERS spectrum intensities with roughness parameters

At this point, we have to indicate what is meant by roughness and its characteristics from the perspective of SERS. Scanning microscopy images of rough, SERS-active, surfaces of Ag, Au and Cu were already presented in an earlier paper [15,17]. In Fig. 1 is shown a SERS active surface of Ag, Au and Cu. 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 and 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 [18] some peculiarities of the SERS emission when a diffraction grating is used as optical coupler. We showed that in the circumstances of an excitation of surface plasmons, the SERS intensity depends on the ratio between grating groove depth and grating periodicity. We also proved experimentally that there is an optimum groove depth of the grating for which Raman efficiency is highest. By idealizing the Ag, Au and Cu surfaces used as active SERS supports, we may assimilate these 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 image 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. 2 which presents results concerning two polymers, poly-3-alkyl thiophene and polyaniline–emeraldine, 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 that of the latter. Operating on the film preparation techniques, we managed to obtain films of different and controlled roughness values, more specifically we obtained a variation of h in the h/a ratio. The results in Fig. 2 were assessed by scanning microscopy. It was found

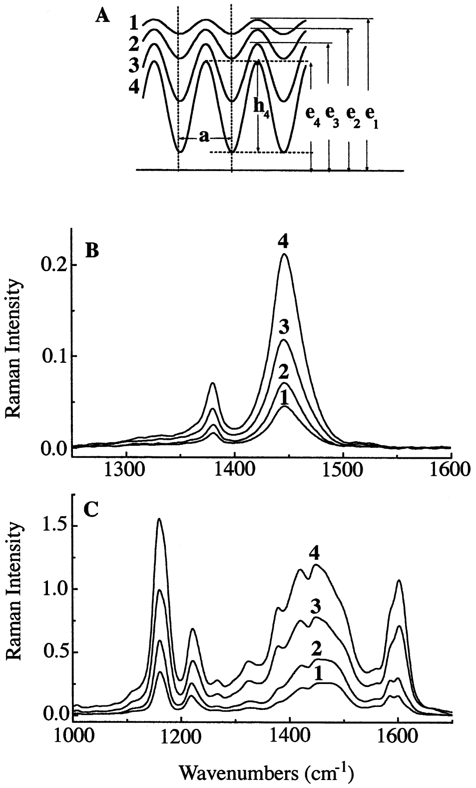


Fig. 2. Roughness dependence of SERS intensities of poly (3-hexyl thiophene) (B) and polyaniline emeraldine structure (C). (A) illustrates an idealized change in the metal support roughness by means of different preparation techniques. Spectra 1–4 from (B) and (C) correspond to the 1–4 roughness profiles in figure (A).

that, keeping the same deposition geometry and changing metal film thickness, the parameter *h* was changed too. The Fig. 2a illustrates an idealized change in metal support roughness by means of different preparation techniques. To obtain a roughness change, 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. For example Fig. 1a can be associated to the roughness profile illustrated by curve 4 in Fig. 2a. The results shown in Fig. 2 are summarized in Table 1 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.

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

The SERS spectra that were recorded on thin films deposited on Ag, Au and Cu metal supports for chemically prepared emeraldine and pernigraniline are shown in Fig. 3a 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 pernigraniline obtained by cyclic voltammetry on Ag and Au electrodes are given in Fig. 3c. Tables 2–4, which were derived from Fig. 3, show the positions of the Raman lines, observed by in situ measurements, and the vibrations associated with them [19,20], 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. 2a,b stay virtually unchanged regardless of the solvent, chloroform or NMP, that had been used to prepare the polymer solutions from which the polymer films were obtained. Two major facts derive from the results of Fig. 3: i) in the case of polymer films ranging from 100 to 200 nm in thickness, SERS spectra of emeraldine are seen to depend on the type of the metal support and ii) in the case of pernigraniline, 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. First, a process of electromagnetic origin occurs, via the excitation of surface plasmons 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 dielectric constant of the metal with the excitation wavelength), its roughness characteristics, and the polymer film thickness. All of these finally result in how the polymer film is ‘seen’ by the evanescent wave. Second, a subtler, harder to understand chemical

Table 1
Variation of the SERS intensity as function of metallic film thickness and roughness parameters

Au film thickness *e* (nm)	Parameter *h* (nm)	Raman intensity		
		Normalized scale (calc.)	Poly(3-hexylthiophene) (exp.)	Emeraldine base (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

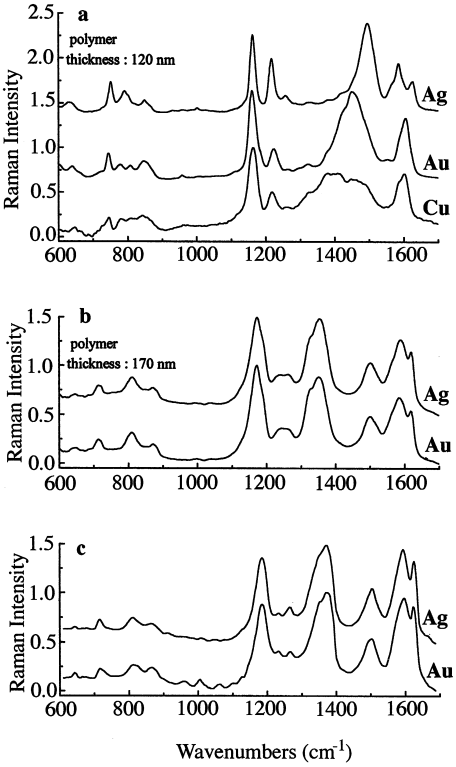
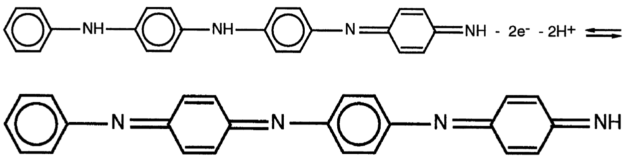


Fig. 3. SERS spectra of polyaniline films: (a) emeraldine and (b) pernigraniline structures prepared by chemical polymerization deposited on rough Ag, Au and Cu supports, (c) SERS spectra of pernigraniline films prepared on Ag and Au electrodes by cyclic voltammetry.

effect can be involved, 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 SERS spectrum generation mechanism should increase as polymer films decrease in thickness. As expected, the SERS spectra of emeraldine and pernigraniline, which differ in oxidation degree, are different from each other. In addition, Fig. 3 shows a new result, namely that the SERS spectra of emeraldine also depend on metal support type. Such a variation actually concerns two distinct aspects: the overall scattered intensity, and the position and relative intensity 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 2 or 5 as we change from Ag to Au, and Cu, respectively. The result may be associated with an electromagnetic excitation origin of the SERS spectra, via the surface plasmons. The second type of SERS spectrum variation with metal support type is only found in emeraldine (Fig. 3a). This variation is a consequence of the oxidizing properties of the metal supports. As mentioned above, emeraldine is a form of polyaniline in which two different basic structures coexist in roughly equal amounts: 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, like in a redox system:



A redox system has an associated redox potential. The reversibility of the A → B process is disturbed by the

Table 2
Vibration modes observed by SERS spectroscopy in Emeraldine base (cm^{-1})

Emeraldine base				Assignments [19]
674.1 nm, Raman spectra, in situ, exp. [19]	Ag	1064 nm, SERS spectra, exp., Au [this work]	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)
1263	1258		1264	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 3
Vibration modes observed by SERS spectroscopy in Emeraldine salt and semiquinoide—radical structure (cm^{-1})

Semiquinoide structure			Emeraldine salt			Assignments
1064 nm, in situ [19]	Calc. [19]	647.1 nm, in situ, exp.	Ag	1064 nm, SERS spectra, chemical polymerisation, Au [this work]	Cyclic voltammetry, Ag/Au	
	1614	1612	1621	1620	1626	C–C stretch (B) + 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)

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 the Form B, thus defining the oxidizing nature of the metal. Hence the reduction process will depend on the type of the 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:

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

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

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

The difference in the 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 if (i) for the polyaniline in oxidized form—i.e., pernigraniline—SERS spectra measured on relatively thick films of 100–200 nm do not depend on metal support type. This is clearly illustrated in Fig. 3b and c where the spectrum of pernigraniline remains unchanged no matter whether Ag or Au is used, and regardless of how the pernigraniline has been prepared, either by chemical synthesis or cyclic voltammetry; (ii) for emeraldine, 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. 3a, particularly at the relative intensities of the bands which have their peaks at ca. 1624 cm^{-1} and 1582 cm^{-1}, associated with C–C stretching deformation in

Table 4
Experimental and calculated vibrational wave numbers in the Raman spectra of polythiophene (PT), 3-POT and 3-PHT

PT [22] υ/cm^{-1}		3-POT [22] υ/cm^{-1}		3-PHT [this work] υ/cm^{-1} exp.	Assignment of vibrational mode [22]
Exp.	Calc.	Exp.	[This work]		
				1624	quinoid structure
1497	1498	1512	1504	1521	$C_{\alpha'}=C_{\beta'}$ stretching
1455	1460	1442	1436	1450	$C_\alpha=C_\beta$ stretching
1365	1359	1378	1376	1378	C_β–$C_{\beta'}$ stretching
	1249	1182	1143		C_β^+–H bending
1224	1210	1210	1202	1210	C_α–$C_{\alpha'}$ stretching
1045	1040			1090	C_β^+–H bending
		1016	1016	997	C_β–C_{alkyl} stretching
740	746	728	723	724	C_α–S–$C_{\alpha'}$ deformation
700	696	682	705	683	Cα–S–$C_{\alpha'}$ deformation
	522	597	586	598	ring deformation

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 turning more strongly oxidized or reduced depending on the metal support should be even more evident if measurements are made on thinner polymer films (ca. 10–50 nm) where the interfacial chemical effect caused by the metal support gets an increased importance in the SERS mechanisms. Fig. 4 shows the results obtained on emeraldine films of ca. 30 nm in thickness. Curve 4 on the same figure presents the SERS spectrum of an 85 nm film of pernigraniline—the oxidized form of polyaniline—deposited on Ag. In Fig. 4, the results illustrate a gradual transformation of the SERS spectra of emeraldine as different metals, Ag, Au and Cu, respectively, are used as supports. The change observed in emeraldine consists in its spectrum growing more alike to that of pernigraniline. 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. 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 and pernigraniline are shown in Figs. 5 and 6. Here again, variations refer to two different aspects: the overall intensity of the Raman radiation, and the positions and especially the relative intensities of certain Raman spectrum lines. 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 and pernigraniline, decreases in virtually direct proportion with the decrease in polymer film thickness. In the lower 50–10 nm range, 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 and pernigraniline, 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, 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 pernigraniline. Pernigraniline 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 re-

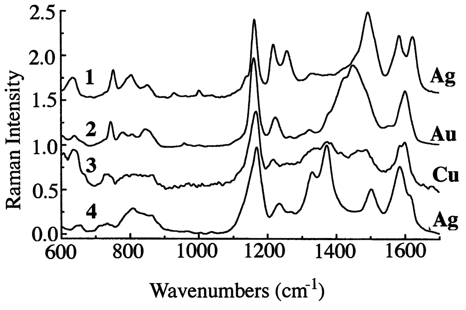


Fig. 4. SERS spectra of emeraldine base films of 30 nm thickness deposited on Ag, Au and Cu (curves 1, 2 and 3, respectively); curve 4 corresponds to the SERS spectrum of 85 nm thickness pernigraniline film.

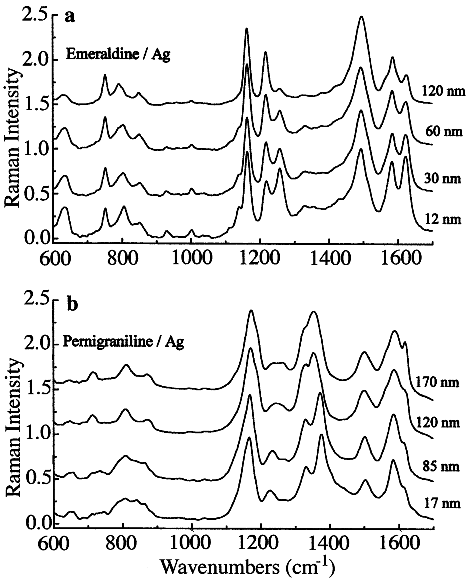


Fig. 5. Thickness dependence of SERS spectra of emeraldine (a) and pernigraniline (b) deposited on rough Ag supports.

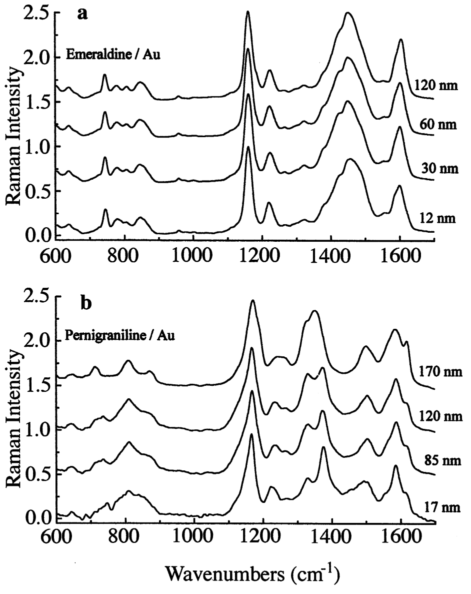


Fig. 6. Thickness dependence of SERS spectra of emeraldine (a) and pernigraniline (b) deposited on rough Au supports.

duced, some changes do occur in pernigraniline 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. 5 and 6. Firstly, it is observed that, for emeraldine, 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: ca. 1624 cm^{-1}, associated with C–C stretching deformation in benzenoid rings; ca. 1582 cm^{-1}, corresponding to –C=C– stretching in the quinoid rings, ca. 1257 cm^{-1} C–H, corresponding to a bending in benzenoid rings, and ca. 1217 cm^{-1}, which corresponds to C–N stretching deformation. Moreover, Fig. 5a 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/Au system where SERS spectra do not change with polymer film thickness (Fig. 6a), one can assume there is no interfacial chemical effect. By contrast, such interfacial effect is evident in the emeraldine/Ag system. A detailed understanding of this effect is not easy for the time being. An invariance of the SERS spectra with metal support type, Ag or Au (Fig. 3b, c), for pernigraniline films in the high thickness range (120 to 170 nm), leads to the conclusion that polyaniline in its oxidized form, i.e., pernigraniline, 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. 5b and 6b, which show that pernigraniline itself undergoes SERS spectrum variation for lower thickness values of the polymer films. In the case of pernigraniline, unlike that of emeraldine, spectrum variation with polymer film thickness does no longer depend on metal support type. Keeping the same thickness of the emeraldine salt film, we find that spectra are virtually identical, no matter whether the metal support is Ag or Au. In this case, too, the SERS spectrum variation with polymer film thickness consists of relative intensity variations in the ca. 1624 cm^{-1} and ca. 1582 cm^{-1} bands. In addition, the SERS spectrum of pernigraniline contains a broad band in the range 1320–1380 cm^{-1}, which is formed by an overlapping of two bands with peaks at ca. 1328 and ca. 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 to the oxidized form of polyaniline. This band has been attributed to semiquinone radical structures, more precisely to C–H bending in quinoid rings (ca. 1328 cm^{-1}) and C–C stretching in quinoid rings, plus C–H bending in benzenoid rings (ca. 1365 cm^{-1}) [19,20]. The coexistence of two bands of different intensities indicates that the distribution of semiquinone radical structures is not uniform [17]. In our case, when polymer film thickness is decreased, the 1365 cm^{-1} band 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, which 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 1328 and 1365 cm^{-1} Raman bands, i.e., a relative exaltation of the 1365 cm^{-1} band associated to 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 polyaniline from its oxidized form to reduced form. As a matter of fact, the latter assertion appears to be confirmed by the variations of the 1624 cm^{-1} and 1582 cm^{-1} bands. Figs. 5b and 6b show that the 1582 cm^{-1} band 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 pernigraniline. 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.

3.3. Interfacial reactions evidenced for SERS on poly (3-hexyl thiophene)

SERS spectra of Fig. 7 are typical for thin films of poly 3-hexylthiophene on Ag or Au obtained from solutions in

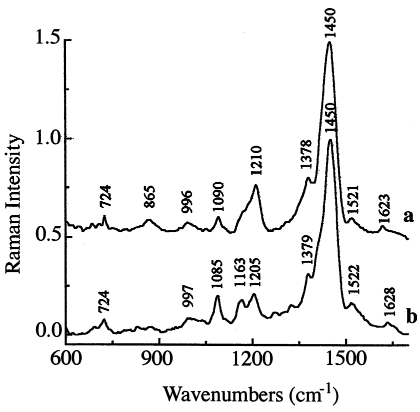


Fig. 7. SERS spectra of poly(3-hexyl thiophene) thin layers deposited on rough Au (curve a) and Ag (curve b).The polymer film of approximately 60 nm thickness was achieved from polymer solution in chloroform.

chloroform. We find that the two spectra are almost identical and are dominated by an intense band with the maximum at 1450 cm^{-1} characteristic of the $C_\alpha = C_\beta$ bond of the thiophene ring. We also observe other Raman emission bands at ca. 724, 865, 997, 1090, 1163, 1210, 1378 and 1521 cm^{-1} whose assignments are shown in Table 4. Besides these bands, the spectrum may contain, in certain conditions, a band with the maximum at ca. 1624 cm^{-1} which is assigned to the quinoid structure. When the thin films of 3-PHT have been prepared from solutions in THF, SERS spectra show some differences, depending on the metal used as support. These differences may be seen in Fig. 8a–c, and are especially manifest in the appearance of the band at ca. 1624 cm^{-1}, associated with the quinoid structure, only when Ag is used as the support of the polymer film. Another feature revealed by Fig. 8, generally observed for conducting polymers irrespective of the type of metallic support, refers to the relative variation of the intensities of some Raman lines with the thickness of the polymer film. With a normalized scale, this fact is illustrated in Fig. 8b, in which the ratio I_{1445}/I_{1624} of the intensities of the corresponding Raman lines decreases from 16 to 4, while according to the calculation the thickness of the polymer film should decrease from 120 to 5 nm. The rate of decrease of the intensities of the SERS bands with the decrease of the polymer film thickness is not constant outside the thickness range 50–200 nm. The decrease of the intensity is proportional to the film thickness in the range 50–200 nm, while for thickness smaller than 50 nm, the decrease is slower and the Raman intensity tends to stabilize asymptotically towards a limiting value. In our opinion, this 'stabilization' of the Raman intensities for small values of the polymer film thickness is a result of the superposition of two effects, the first determined by the morphology of the surface of the metallic support, namely the specific shape and dimension of the roughness, and the second by a possible chemical reaction between the metallic support and the polymer or the solvent molecules. The stabilization effect has been observed for SERS spectra of 3-PHT deposited on Ag or Au from solutions of chloroform or tetrahydrofuran. In the case of the thin films obtained from chloroform, we observe from Fig. 7 that the SERS spectra are almost identical, irrespective of the type of metallic support used, the ca. 1624 cm^{-1} band associated with the quinoid structure being present in both spectra. This fact allows us to consider the coexistence of two structures in the thin films of 3-PHT, one reduced and the other oxidized, the relative importance of the latter being very small. By comparing the results of Fig. 7 with those of Fig. 8, corresponding to the SERS spectra measured on thin films of 3-PHT obtained from solutions of chloroform and tetrahydrofuran respectively, we observe that in the latter, the Raman bands specific to the quinoid structure appear only if Ag is used as the metallic support. In the following, we shall try to explain this fact as a result of the metal–solvent interfacial reactions that lead to the formation of intermediary compounds on which the polymer molecules are adsorbed. A similar mechanism, based on interfacial reactions, was also used for the explanation of the kinetics of electrogeneration of the polypyrrole films on Ag, Au and Pt electrode surfaces [13,14]. In the case of 3-PHT films obtained from solutions in chloroform on rough Ag and Au supports, two chemical reactions may exist between the solvent and the metal supports. These reactions, written below, take place spontaneously and depend on the ionization energies of the metals involved:

$$4Ag + 2CHCl_3 \rightarrow 4AgCl + C_2H_2Cl_2 \quad E_{Ag/Ag+} = 7.57\,eV \tag{1}$$

$$4Au + 2CHCl_3 \rightarrow 4AuCl + C_2H_2Cl_2 \quad E_{Au/Au+} = 9.22\,eV \tag{2}$$

We remark here that the ionization energies of Ag and Au are relatively close to each other (see Eqs. (3) and (4) for comparison). The above equations represent in fact the possible transformations that lead to the formation of stable chemical combinations at the interface, with Ag and Au in the following electronic states:

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

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

Finally, on these combinations resulted from metal–solvent interfacial reactions, the molecules of 3-PHT are deposited as a result of a chemical reaction that leads to

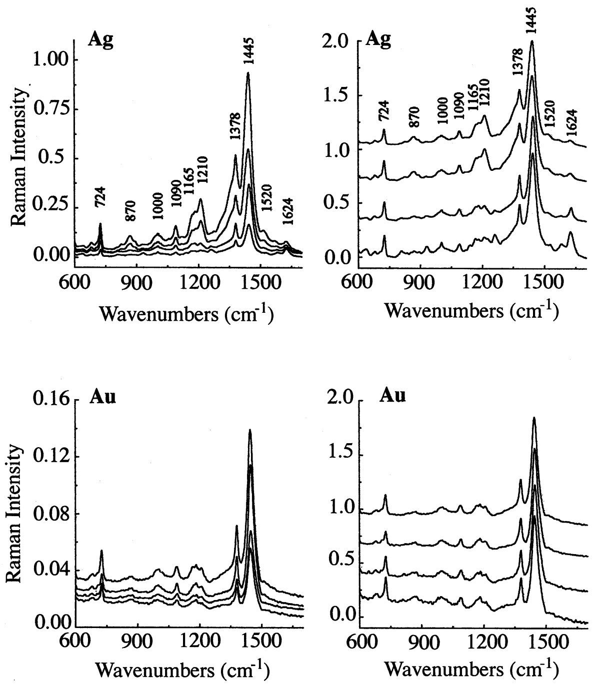


Fig. 8. SERS spectra of poly(3-hexyl thiophene) films obtained from solutions of polymer in tetrahydrofuran. The polymer film thicknesses are 5, 30, 60 and 120 nm with corresponding curves from bottom to top.

the formation at the surface of the metal support of some compounds (see Fig. 9) with coordinative bounds between the S atoms of 3-PHT and the metallic ions, Ag and Au respectively. The formation of the coordinative bounds between the S atom and AgCl, or S and AuCl, leads to the appearance of complex combinations in which Ag and Au have equivalent electronic structures, [Kr]$4d^9$ and [Xe]$4f^{14}5d^9$, respectively. In our opinion, this fact would justify the existence of an equal probability, for Au and Ag, of observation in the SERS spectra of the quinoid structure as well. This result is confirmed experimentally by the close similarity of the two spectra of Fig. 7, in which the band associated to the quinoid structure at 1624 cm^{-1} appears with approximately equal relative intensities. SERS spectra of 3-PHT deposited on Ag and Au from solutions in THF depend on the type of the support. Indeed, Fig. 8 shows that the band associated to the quinoid structure is observed only if Ag is used as the metal support. This different behaviour of the SERS spectra may be explained, by the reasoning already used above, as a result of a chemical process of interaction between the solvent and the metal, that takes place in two stages. In the first stage, the solvent THF reacts with the rough Ag or Au film according to the equations:

$$2Ag + C_4H_8O \rightarrow Ag_2O + C_4H_8,$$

$$E_{Ag/Ag+} = 7.57\,\mathrm{eV} \qquad (3)$$

$$2Au + 3C_4H_8O \rightarrow Au_2O_3 + 3C_4H_8,$$

$$E_{Au/Au3+} = 30.5\,\mathrm{eV} \qquad (4)$$

We see that in this case the ionization energies of the metals used as supports are large. The reactions (3) and (4) take place in the specified direction and involve a stable electronic state for Ag:

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

and, for Au, an electronic state much more unstable than that mentioned in Eq. (2), namely:

$$Au - 3e^- \rightarrow Au^{3+} \quad [Xe]4f^{14}5d^{10}6s^1 - 3e^- \rightarrow [Xe]4f^{14}5d^8$$

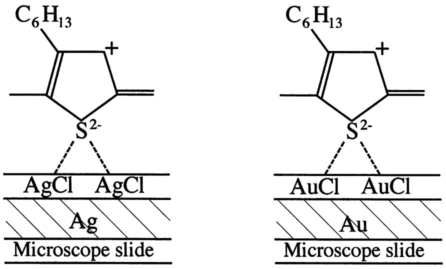


Fig. 9. Model of the chemical reactions taking place on the Ag and Au surfaces when the chloroform is used as solvent.

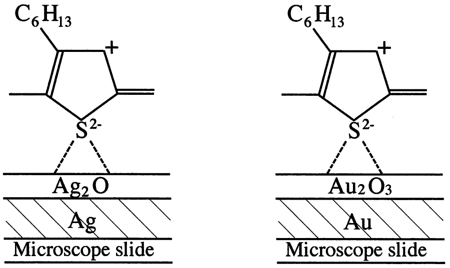
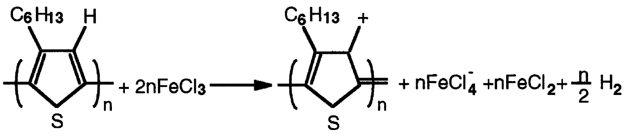


Fig. 10. Model of the chemical reactions taking place on the Ag and Au surfaces when the tetrahydrofuran is used as solvent.

In the second stage, 3-PHT is adsorbed on the layer of Ag_2O, respectively Au_2O_3, as in Fig. 10. We observe that the formation of a coordinative bond between the sulfur atom of the thiophene ring and Ag_2O, respectively Au_2O_3, leads to complexes in which Ag and Au will have different electronic structures, namely [Kr]$4d^9$ and [Xe]$4f^{14}5d^7$. The realization of a stable state of the type d^{10} requires in this case a smaller energy for Ag than for Au, which could explain the absence of the quinoid structure in the SERS spectra of 3-PHT on Au support when the thin films are obtained from solutions in THF.

3.4. SERS spectra of 3-PHT in doped states

The study of the doping effect of 3-PHT was realized on thin polymer films of approximately 60 nm deposited on rough Au supports. The thin polymer films were obtained by the procedure of the evaporation of the solvent explained above, by using solutions in chloroform and tetrahydrofuran. The doping was done by adding a certain volume of solution of $FeCl_3$ in acetonitrile with pre-established concentration to a known volume of solution of 3-PHT in chloroform or tetrahydrofuran. The increase of the degree of doping was achieved by increasing the quantity of $FeCl_3$ added to the same volume of polymer solution. We have recorded SERS spectra for the unoxidized state and different oxidized states. The oxidized states were prepared starting from a polymer solution in chloroform of 0.1 wt.% concentration in which was added 0.1 cm^3 from a solutions of $FeCl_3$ in CH_3CN of concentrations 0.02 M, 0.05 M, 0.07 M and 0.1 M respectively. The global doping reaction is:



For the samples obtained in this way, the result of the gradual doping of polymer leads to the SERS spectra shown in Fig. 11, the bottom curve corresponding to the undoped state. Using for the average gravimetric molecular weight the value Mn = 8370 g/mole, one can estimate that the degree of polymerization of 3-PHT used in this

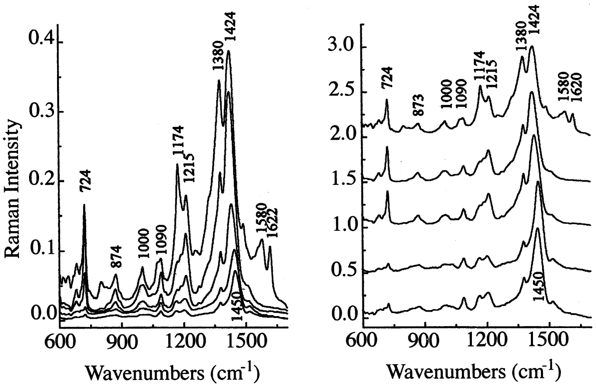


Fig. 11. The oxidation effect of the poly(3-hexyl thiophene) observed by SERS spectroscopy. The polymer thin layers of approximately 60 nm thickness were deposited on rough Au support from polymer solutions in chloroform. The undoped state and doped states for 8, 16, 34 and 50 units correspond to curves from bottom to top. The whole molecular chain is estimated to 50 units. For the right figure is used a normalized scale.

work is about 50. By increasing the quantity of $FeCl_3$ added to the same quantity of polymer solution, one obtains a gradual increase of the doping of the macromolecular chain with $FeCl_4^-$ ions, and one can even estimate the number of doped structural units. We estimate that by using the doping procedure indicated above the number of doped units is 8, 16, 34 and 50, that is 16%, 32%, 68% and 100%, with corresponding curves on Fig. 11 from the second to the top one. The results of Fig. 11 lead to the following remarks. The doping of the polymer determines in general an increase of the intensity of the Raman spectrum with respect to the undoped state. The gradual increase of the doping degree. induces both an increase of the 1450 cm^{-1} intensity band and a gradual shift of its peak to lower energies, ca. 1424 cm^{-1}. This reveals a modification of the vibration frequency specific to the bond $C_\alpha = C_\beta$ in the thiophene ring by the passage from the reduced state ca. 1450 cm^{-1} to the oxidized state ca. 1424 cm^{-1} [21]. The passage to the oxidized state also modifies the relative intensities of some bands in the Raman spectrum of 3-PHT. By oxidation, one observes an important increase of the intensity of the band at ca. 1210 cm^{-1} corresponding to the bond C_α–$C_{\alpha'}$ characteristic to the head–tail structure, and of the band at ca. 724 cm^{-1} associated to the deformation of the bond C_α–S–$C_{\alpha'}$. These results lead to the conclusion that in the doped state of the macromolecular chain of 3-PHT appear steric effects due to the two voluminous substituents $FeCl_4^-$ and the hexyl radical. In this case, the interatomic distances are relatively small and consequently in the interaction C_α–$C_{\alpha'}$, the repulsion prevails. This fact may explain the instability of the screened positions in which the interatomic distances are minimum. The instability imposes the passage of the macromolecular chain in a staggered conformation that corresponds to the minimum of the potential energy. An interesting result is the appearance of the band at 1622 cm^{-1} associated to the quinoid structure, the maximum intensity of this band being observed for the doping degree 100%. We remark here that qualitatively, the results of Fig. 11 are entirely similar to those obtained for poly 3-octylthiophene (3-POT) [21]. In Section 3.3, we have shown that the SERS spectra of 3-PHT thin films obtained by the evaporation of the solvent depend on the type of solvent and on the type of metal used as support. The results of Figs. 11 and 12 show that this dependence also exists when the polymer is in an oxidized state. The gold was used as support in both cases. The spectra of Fig. 12 belong to the thin films of 3-PHT obtained from solutions in THF. The most important difference that exists between Figs. 11 and 12 is the absence from the latter of the Raman band at 1622 cm^{-1}, associated with the quinoid structure. A interesting conclusion follows from this, namely that the observation of the quinoid structure in the SERS spectra of 3-PHT, whether in a reduced or oxidized state, also results from metal–solvent interfacial reactions of the type illustrated in Section 3.3, Figs. 9 and 10. It is known that the Raman lines of ordered systems have Lorentzian profiles, and that the passage to disordered or inhomogeneous systems is accompanied by an asymmetrical modification in the lower energy wing of the Raman profile, by addition of a Gaussian component. A typical example of an order–disorder transformation of the Raman line profile appears in the passage of silicon from the crystalline (ordered) state to the porous or amorphous (disordered) state [23]. The further examination of Figs. 11 and 12 shows that in the SERS spectra of 3-PHT, the profiles of the Raman lines of the oxidized state are different from those of the reduced state. For the reduced state, the best fit is generally obtained with a Lorentzian profile for each Raman line. A careful analysis of the

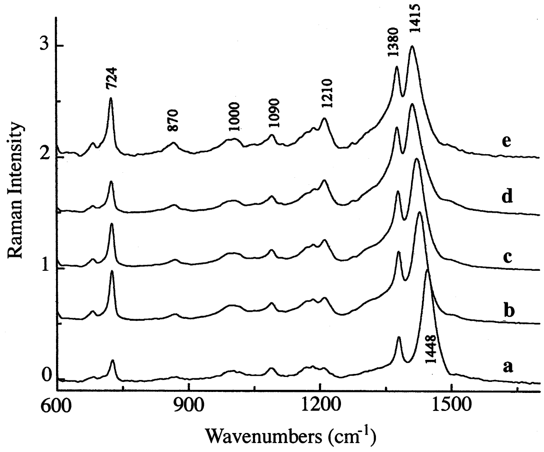


Fig. 12. The oxidation effect of the poly(3-hexyl thiophene) observed by SERS spectroscopy. The polymer thin layers of approximately 60 nm thickness were deposited on rough Au support from polymer solutions in tetrahydrofuran. The undoped state and doped states for 8, 16, 34 and 50 units correspond to curves from bottom to top. The whole molecular chain is estimated to 50 units.

spectra of Figs. 11 and 12 shows that by the doping of 3-PHT, one also obtains a modification of the profiles of the Raman lines, similar to that obtained in the transition to a disordered state. Apart from this, in the case of thin polymer films obtained by the evaporation of the solvent, we find that the state of disorder established by the doping process depends on the type of solvent in which the polymer was dissolved and on the type of metal on which it was deposited. The comparison, from this point of view, of the results obtained with the polymer films of same thickness, prepared from more clearly the gradual establishment of disorder when the degree of doping is increased. This is clearly observed by SERS spectroscopy. This effect observable on whole spectrum is further illustrated in Figs. 13 and 14, corresponding to the spectral ranges ca. 650–800 cm^{-1} and ca. 1250–1600 cm^{-1} respectively. From Fig. 13, it follows that the doping process leads to the a symmetrization of the band with the peak at ca. 724 cm^{-1} by the appearance in the lower energy wing as a new band, having a Gaussian profile with the maximum at ca. 709 cm^{-1}. Similar and more convincing results are presented in Fig. 14. The spectra presented in this figure correspond to the spectral range in which the Raman lines of 3-PHT have the greatest intensity. We find that even for the reduced state (Fig. 14a), the best fit is obtained with a Lorentzian profile for each Raman line from ca. 1445 cm^{-1} to ca. 1380 cm^{-1}, convoluted with a Gaussian profile of much lower intensity centered at ca. 1320 cm^{-1}. Several measurements fulfilled on reduced state samples deposited on metallic supports with different roughness show that this disorder, that is the intensity of the Gaussian component, is little dependent on the roughness of the metal support but rather on the polymer layer thickness. Regarding now the spectra of the doped 3-PHT (Fig. 14a–c), we clearly find that by increasing the degree of doping, the SERS spectra are gradually modified and the best fit is obtained with a Lorentzian profile for each Raman line from ca. 1445 cm^{-1} to ca. 1380 cm^{-1} convoluted with a growing up Gaussian band which is associated to a disorder state in the molecular chains. Apart from this, the following facts are worth mentioning: (i) a shift of the principal maximum at ca. 1445 cm^{-1} to lower energies, with a tendency to stabilize its position at about 1415 cm^{-1} for degree of oxidation of 100%; (ii) an increase of the relative weight of the Gaussian component and a simultaneous shift of its maximum from ca. 1320 cm^{-1}, corresponding to the reduced state, to ca. 1385 cm^{-1}, when the completely doped state is achieved and (iii) an a gradual change of the ratio of the intensities of the ca. 1445 and ca. 1380 cm^{-1} lines, in the favour of the latter,

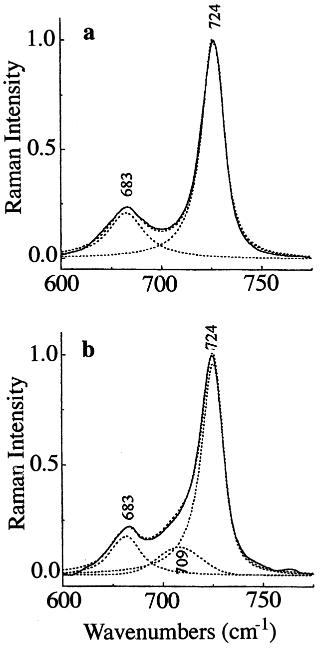


Fig. 13. The oxidation effect on SERS spectra of the poly(3-hexyl thiophene) thin layer (approximately 60 nm thickness) deposited from solutions in tetrahydrofuran on Au rough film; (curves a and b correspond to non-oxidized and 100% oxidized form respectively).

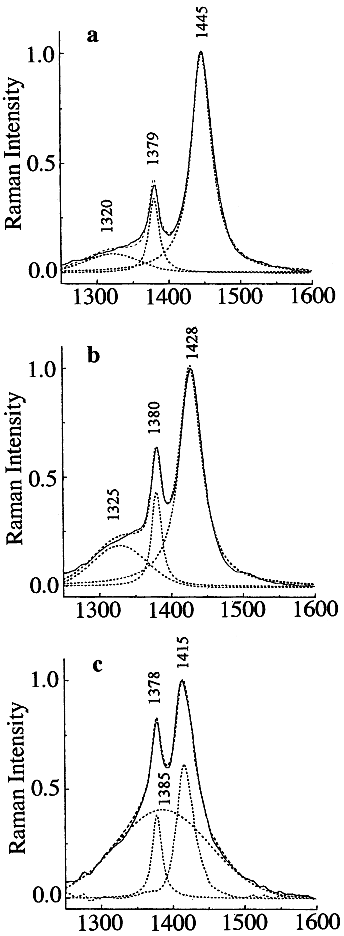


Fig. 14. The oxidation effect on SERS spectra of the poly(3-hexyl thiophene) thin layer (approximately 60 nm thickness) deposited from solutions in tetrahydrofuran onto Au rough film; (curves a, b and c correspond to non-oxidized, 16% and 100% oxidized form respectively).

which is associated to a disorder state in the molecular chains We ascertained that the intensity of the effect of induced disorder in the macromolecular chain by oxidation process depends also on the type of metal used as support and on the type of solvent from which the thin polymer films have been prepared. This dependence suggests that metal–solvent interfacial reactions are also involved.

3.5. SERS spectra on carbon nanotubes

Single walled carbon nanotubes (SWNT's) were prepared according to the electric arc method, under the conditions described in Ref. [24]. They were firstly ultrasonicated in solvent (ethanol, chloroform) and in a second step, deposited on a rough metallic surface (Au or Ag). By comparing the estimated weight of sample studied ($\cong 0.1$ μg) to the weight of sample studied in standard Raman experiments, the enhancement of the overall SERS signal is expected to be of the order of three orders of magnitude. The SERS spectrum of carbon SWNT's is presented in Fig. 15. Three different frequency regions can be distinguished. Between 1500 and 1600 cm^{-1}, two main bands are peaked at 1594 and 1572 cm^{-1} while shoulders are clearly observable at 1556 and 1540 cm^{-1}. There results are close to those obtained by Kasuya et al. [25] and related to the curvature of the graphene sheet, the consequence of which being the splitting of the E_{2g2} graphite mode [26,27]. The additional components are presumably contributions from SWNT's of different radius. In the low frequency region, an intense peak is recorded at 165 cm^{-1}, with a shoulder at 178 cm^{-1}. These bands are assigned to the A_{1g} breathing mode of SWNT's, where frequency decreases where the tube diameter increases. This result is quite unusual since it has been shown clearly [28] that many different components are observed in these frequency regions, as a result of a broad diameter distribution for SWNT's. We think that in this case, a highly selective resonant enhancement can explain the predominance of 165 cm^{-1} A_{1g} mode associated to a (10,10) armchair tube. In the intermediate rouge, a peculiar mode is observed at 1270 cm^{-1}, which exhibits an asymmetric profile in its low frequency side. This mode is usually assigned to a disorder structure with a nanometric size, such as carbon nanoparticules, amorphous carbon or defects in SWNT's. We have tested the presence of amorphous carbon in our samples and recorded their SERS spectra under similar conditions. we think, as a result, that both a.C and defects on SWNT's contribute to this additional 1270 cm^{-1} Raman band. More details will be published elsewhere [29].

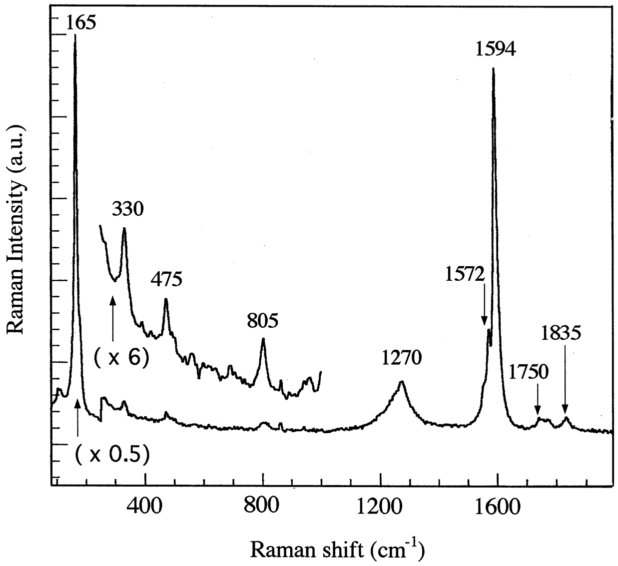


Fig. 15. SERS spectrum of SWNT's deposited on a rough Au surface, recorded at room temperature with a laser excitation $\lambda_{exc.} = 1064$ nm.

4. Conclusions

The 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 metal/dielectric (polymer) interface, which in turn depend on the types of metal, including here its surface roughness, and dielectric that are in contact. Hence a first conclusion, namely that the identification of an interfacial chemical process is no longer of the same generality degree as the one implied by the electromagnetic exaltation mechanism. The SERS studies reported in this paper were carried out under 1064 nm laser excitation. Our goal was to identify the chemical effects at polymer/metal interface that are involved in specific SERS spectrum modifications. The following results have been obtained: i) using the scanning microscopy images of SERS-active surfaces, we try to indicate more precisely what is meant by roughness and its characteristics from the perspective of SERS. 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 optical coupler; ii) SERS spectra of emeraldine were shown to depend on the type of the metal support, namely Ag, Au or Cu. This dependence stems from a double origin: an electromagnetic one, via the surface plasmons which are associated as the Raman scattered intensity changes with metal support type; and a chemical one, revealing an oxidation of emeraldine, at the polymer/metal interface; iii) SERS spectra of pernigraniline remain unchanged when the metal support is changed, which proves the stability of the oxidized form; iv) the SERS spectrum variation with polymer film thickness has revealed an electron delocalization taking place in the pernigraniline molecule, as a result of an electron transfer from metal to the polymer molecule on the level of the quinoid ring; v) the SERS spectra of poly(3-hexyl thiophene) thin films deposited by the evaporation of the solvent on rough Ag and Au supports depend on the oxidizing properties of the metal surface and on the nature of the solvent. This dependence determines the existence of two types of successive reactions. The first reaction takes place at the metal–solvent interface and results in an interface compound of the type MeX (Me = Ag or Au, X = Cl or O). The second reaction takes place between the MeX interface compound and the polymer, so that in the end, the structure of the surface is metal–interface compound–polymer. This structure can explain the fact that the intensity of the quinoid band in the SERS spectra depend on the type of the metal used as support and on the nature of the solvent in which the polymer was dissolved; vi) SERS spectra of doped 3-PHT reveal the increase of the intensities of the Raman lines, accompanied by the modification of the intensity ratios when the degree of doping is increased; vii) in the SERS spectra of 3-PHT, the profiles of the Raman lines of the oxidized state are different from those of the reduced state. The reduced state corresponds to an ordered system for which the Raman lines have a Lorentzian profile. The passage to disordered or inhomogeneous systems is accompanied by an asymmetrical modification in the lower energy wing of the Raman profile, by the addition of a Gaussian component. We observe by SERS spectroscopy that the passage to the doped state of 3-PHT is accompanied by the establishment of a disordered state in the structure of the macromolecular chain, as a result of steric hindrance effects.

In addition to these results obtained for the first time for conjugated polymers, we have shown that SERS spectra of carbon single walled nanotubes exhibit peculiar features. Firstly, the low frequency breathing mode is predominantly peaked at 1654 cm^{-1}, putting in evidence strong resonance effects for nanotubes of a specific diameter. Secondly, an additional feature at 1270 cm^{-1} can be interpreted as due to both amorphous carbon in real small amounts, as well as to defects on the nanotubes. SERS is proved to be, one more time, of significant importance in the study of carbon SWNT's deposited in the form of thin films on rough metallic surfaces.

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