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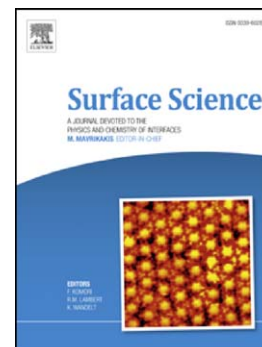
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## Spectroelectrochemical Behaviour of 4-Aminobenzenethiol on Nanostructured Platinum and Silver Electrodes

F. J. Vidal-Iglesias, J. Solla-Gullón, A. Rodes, J. M. Feliu\* and J. M. Pérez\*

Instituto de Electroquímica, Universidad de Alicante, Ap 99, 03080 Alicante

\* juan.feliu@ua.es Tel. +34 965909301

\* jmpm@ua.es Tel. +34 965903927

### Abstract

The adsorption of 4-aminobenzenethiol (4-ABT) on Ag and Pt nanoparticles is studied by spectroelectrochemical means (cyclic voltammetry, Surface-Enhanced Raman Spectroscopy (SERS) and Surface-Enhanced Infrared Reflection Absorption Spectroscopy (SEIRAS). Similar SERS spectra are obtained when 4-ABT is adsorbed on platinum and silver nanostructured substrates. In addition, unless a low power density of the laser is used, these spectra show, both under open circuit conditions and when applying electrode potentials above -0.50 V, bands not observed in the normal Raman spectrum of 4-ABT. These bands disappear when the electrode potential is shifted to more negative values. Conversely, the SEIRA spectra of 4-ABT adsorbed on Ag do not show any significant change with the electrode potential, which indicates that there are not new species electrochemically formed in the range of potentials considered, which include some anodic and cathodic processes as shown in the corresponding cyclic voltammograms. In this regard, SERS measurements put in evidence the time dependence of the spectra obtained at potentials above -0.50 V just after switching on the laser suggesting the formation of new species, probably dimercaptoazobenzene (4-4'-DMAB), formed by a photochemical process of the adsorbed 4-ABT.

**Keywords:**

SERS, SEIRAS, aminobenzenethiol, dimercaptoazobenzene, Pt nanoparticles, Ag nanoparticles

**1. Introduction**

Raman spectroscopy is a widely used technique. Although it is relatively insensitive to free molecules, especially in dilute solutions, adsorption of molecules on nanostructured metal surfaces can result in a very large increase in sensitivity. This Surface Enhanced Raman Scattering (SERS) was first observed in 1974 [1]. Noble metal nanostructures exhibit a surface-enhanced Raman scattering in which the scattering cross sections are dramatically enhanced for molecules adsorbed thereon [2]. This enhancement factor can be in the order of  $10^4$ - $10^{14}$  [3] in comparison to that present in the adsorption on a metallic smooth surface although the claim of extremely high enhancement factors of  $10^{14}$  in single-molecule SERS is critically discussed, in particular in the view of recent experimental and theoretical results that limits the electromagnetic enhancement to  $10^{11}$  [4]. It is generally accepted that two different mechanisms must be involved in SERS: electromagnetic (EM) and chemical or charge transfer enhancement (CT). The electromagnetic theory is based on the excitation of localized surface plasmons while the chemical theory assumes the formation of charge-transfer complexes [2, 5, 6]. Nano-irregularities allow surface plasmon resonance, resulting in a very strong local enhancement of the electric field of both incoming and scattered radiation that explains, moreover, that the enhancement extend to at least 10 nm away from the metallic surface. Only coinage metals such as Ag, Au and Cu cause a strong enhancement of the

Raman scattering due to the favourable characteristics of their dielectric functions. Most other metals, including catalytic metals such as Pt or Pd are commonly considered as non-SERS actives because the efficient excitation of surface plasmon is unfavourable on such highly damping metal surfaces [7-10]. However, by suitable methods (among them the oxidation-reduction cycling [11] and nanoparticle-on-electrode approach [12]) an adequate surface morphology is made and a sufficient enhancement is produced to allow SERS spectra from these metals to be obtained. On the other hand, the exact origin of the chemical contribution to the enhancement of the Raman scattering remains an active area of research both from a theoretical and experimental points of view. The most studied mechanism for the chemical enhancement is the so-called charge-transfer mechanism that in turn implies three types, being the two most considered the formation of a surface complex either by direct binding to the metal or by indirect binding with the assistance of an electrolyte ion. A photon-driven charge transfer between analyte and metal has been also considered. While the chemical effect is weaker in magnitude than the electromagnetic enhancement, there is a possibility in some cases that the charge-transfer contribution may dominate the SERS spectrum. In the case of the Pt-group metals this chemical enhancement component should play a very important role, to compensate for their highly damping metal surfaces [7-10].

The formation of self-assembled monolayers (SAMs) has been extensively used for solid surfaces as a simple and versatile way to define the chemical composition and structure of a surface modification. Among them, SAMs based on aromatic thiols have been vastly studied [13, 14]. The formation of organic monolayers by self-assembly is directed by a specific interaction between a terminal functional group and the surface, in this case, the bond formed between the thiol sulphur and the metal. Research has been particularly interested in amino-terminated monolayers because they have been used for

several applications such as the attachment of carbon nanotubes on metal surfaces [15, 16] and the binding of biomolecules, such as DNA [17, 18]. Aminobenzenethiols (ABT) are frequently studied as SERS probe molecules [19, 20] and particularly 4-ABT is widely used as molecular junction [21, 22] and building block in SAMs [21, 23]. A huge amount of work has been reported about the 4-ABT adsorption on Ag and Au due to the same specific behaviour under certain experimental circumstances. Nevertheless, the SERS from the self-assembled monolayer of 4-ABT on Ag and Au is significantly different from the normal Raman spectrum of the molecule in solid state. In normal Raman spectrum only bands that correspond to completely symmetric  $a_1$  vibrations are observed, whereas in its SERS spectrum, non- $a_1$ -type bands ( $1142\text{ cm}^{-1}$ ,  $1390\text{ cm}^{-1}$  and  $1432\text{ cm}^{-1}$ ) are also present under open circuit conditions [24, 25] or when applying high enough electrode potentials [26, 27]. However, SERS spectra from benzenethiol on these metals are substantially the same as the normal Raman spectrum. It was speculated [24, 25] that the alteration of the spectrum of 4-ABT could be due to the contribution of the CT mechanism in enhancement, as a consequence of the alteration of electronic states of benzenethiol by the introduction of an  $\text{NH}_2$  group in the benzene ring. Alternatively, it was also shown, based on the spectral similarity of 4-ABT and dimercaptoazobenzene (4,4'-DMAB), that the non- $a_1$ -type bands correspond to  $\text{N}=\text{N}$  stretching vibrations of 4,4'-DMAB produced from 4-ABT via a photocatalytic coupling reaction [26, 27]. On the other hand, both CT and EM enhancements in SERS of 4-ABT adsorbed onto assemblies of Au(core)/Cu(shell) nanoparticles was separately analyzed [28]. The formation of the azo-derivative observed in the cases of Au and Ag surfaces was recently claimed to be not observed on a Cu surface [29] activated by oxidation-reduction cycling, pointing out that the nature of the metal could also play an important role in the azobenzene derivative formation.

Apart from the controversy over the possible contribution of the chemical mechanism in the SERS of 4-ABT adsorbed on Ag, Au and Cu, in our knowledge the spectroscopic behavior of this molecule adsorbed on other metallic materials of both fundamental and practical importance as the Pt-group metals has received little attention due to their inefficient excitation of surface plasmon on such a highly damping metal surface under conditions of visible wavelength. The formation of a SAM of 4-ABT on polycrystalline platinum electrodes has been characterized by surface analysis and electrochemical techniques [30] and it was concluded that the 4-ABT is adsorbed on the Pt surface through the sulphur atom, forming S-Pt bonds and giving an amino-terminated SAM. However, the presence of the 4,4'-DMAB or the non- $a_1$ -type bands ( $1142\text{ cm}^{-1}$ ,  $1390\text{ cm}^{-1}$  and  $1432\text{ cm}^{-1}$ ) was surprisingly not mentioned. On the other hand, Ag nanoparticle-mediated Raman scattering measurements were conducted by Kim et al. [31] for 4-ABT monolayers assembled on a macroscopically smooth Pt substrate [31] at open circuit potential. In this case non- $a_1$ -type bands are also recorded. An electromagnetic coupling of the localized surface plasmon of Ag nanoparticles with the surface plasmon polariton of the Pt substrate is claimed to explain the SERS spectra observed while from the excitation wavelength dependence a contribution of the charge-transfer enhancement that become more important at short-wavelength excitation is also proposed.

In this manuscript we study, for the first time, the adsorption of 4-ABT on Pt nanoparticles by spectroelectrochemical means (cyclic voltammetry, and SERS) and we compare it with that on Ag. The particular effect of power density of the laser employed in the SERS measurement is also evaluated. We study by Surface Enhanced Infrared Absorption Spectroscopy (SEIRAS), also for the first time, whether new species can be formed by varying the electrode potential without laser excitation when silver is used as

substrate. Finally, we perform time dependent SERS measurement in order to support the participation of a photochemical (or photothermal) process of the adsorbed 4-ABT affected by the energy density of the laser.

## 2. Experimental

### 2.1 Electrochemical measurements.

Electrochemical measurements were performed in 0.1 M NaClO<sub>4</sub> or in 0.1 M NaClO<sub>4</sub> + 10<sup>-3</sup> M 4-ABT solutions at room temperature. Working solutions were daily prepared from Millipore Milli-Q water (18.2 MΩ·cm), sodium perchlorate (Merck, p.a.) and 4-ABT (97% Aldrich). Solutions were deaerated with Ar (N50, Air Liquide). A three-electrode electrochemical cell was used. The electrode potential was controlled using a PGSTAT302N AUTOLAB system. The counter electrode was a Au wire and the working electrode was a polyoriented Pt or Ag bead electrode which was flame annealed before taking it into the electrochemical cell. Potentials were measured against an AgCl/Ag reference electrode connected to the cell through a Luggin capillary.

### 2.2 Spectroscopic measurements.

SERS measurements were performed using the so-called nanoparticles-on-electrode approach [12, 32-34]. For SERS experiments the nanostructured electrode was made by depositing a droplet of a metal nanoparticle aqueous suspension with a pipette onto a polycrystalline polished Pt, Ag or glassy carbon disk (2mm in diameter) sheathed in a threaded PTFE piece. The droplet was dried in air for ~30 min. This substrate was then mounted on an electrochemical poly(tetrafluoroethylene) (PTFE) flow cell specifically designed for the in situ Raman measurements. A saturated Ag/AgCl electrode was used as reference electrode and a Pt wire was used as counter electrode. Raman spectra were

obtained with a NRS-5000 Laser Raman Spectrometer (Jasco). The excitation line was provided by a 17 mW He–Ne laser at 632.8 nm (for Pt) or a 50 mW Nd-YAG laser at 532 nm (for Ag). The laser beam was focused through a 50×longworking distance objective (0.5NA) into a 2  $\mu\text{m}$  spot at the electrode surface. The spectrometer resolution was better than 5  $\text{cm}^{-1}$  and the detector was a Peltier cooled charge coupled device (CCD) (1064×256 pixels).

The internal reflection infrared spectroscopy experiments were performed in a glass spectroelectrochemical cell [35] equipped with a prismatic germanium window beveled at 60° and using a gold wire as the counter electrode and a AgCl/Ag electrode as the reference electrode. A silver thin film chemically deposited on the germanium prism was used as the working electrode. These films were prepared by immersing the Ge substrate for 10 min in a solution formed by mixing 50  $\mu\text{L}$  of a 0.02 M hydrazine solution with 10 mL of a 0.01 M silver nitrate solution containing ammonium hydroxide (0.46 M) and EDTA (0.14 M) [36] (all chemicals “pro analysis” quality from Merck). Under these conditions, a bright thin silver film was formed. After 5 min, the desired deposition time, the sample was removed from the silver-containing solution, rinsed with plenty of ultrapure water, and dried in an argon (N50) stream. Thickness of the silver film formed under these conditions was estimated to be around 10 nm from ex-situ Atomic Force Microscopy (AFM) measurements [35]. All the infrared spectra are presented in absorbance units (a.u.) and were obtained with a resolution of 8  $\text{cm}^{-1}$  with a Nexus 8700 (Thermo Scientific) spectrometer equipped with a MCT-A detector. Sets of 100 interferograms were collected at increasing sample potentials in the 4-ABT-containing solution and plotted in absorbance units as  $-\log(R/R_0)$ , where  $R_0$  represents and referred to a reference single beam spectrum obtained from the same number of interferograms collected at -1.0 V before dosing 4-ABT.



### 2.3 Synthesis of nanoparticles.

Pt nanoparticles (PtNP) were synthesized in a water-in-oil microemulsion (water (3%) / polyethylene glycol dodecyl ether (Brij®30) (16.5 %) / n-heptane (80.5%)), being  $\text{H}_2\text{PtCl}_6$  the platinum precursor and using a similar methodology to that previously reported [37]. The values in brackets show the volume percentage of each compound. Sodium borohydride was used as reducing agent in a  $\text{NaBH}_4$  / Pt molar ratio of 10/1. After the synthesis, the nanoparticles were cleaned employing the protocol described previously [38]. This procedure allows the cleaning of the nanoparticles while avoiding electrochemical adsorption of oxygen and thus preserving the initial surface structure of the nanoparticles.

The synthesis of Ag nanoparticles was performed adapting a classical method for the synthesis of gold nanoparticles [39]. In brief, a 20 mL water solution of the metallic precursor ( $2.5 \times 10^{-4}$  M  $\text{AgNO}_3$ ) was reduced with ice-cold sodium borohydride (0.6 mL, 0.1 M) in the presence of sodium citrate ( $2.5 \times 10^{-4}$  M), which acts as stabilizer. Afterwards, a NaOH pellet ( $\approx 0.2$  g) was added to make the nanoparticles precipitate. After complete precipitation, the nanoparticles were collected and washed 3–4 times with ultrapure water.

## 3. Results

### 3.1 SERS study

Figure 1 shows the voltammetric profiles for silver and platinum massive electrodes in contact with a 0.1 M  $\text{NaClO}_4$  +  $10^{-3}$  M 4-ABT solution in the potential window of interest for the SERS experiments. In the voltammetric experiments, the working electrode contacted the working solution at open circuit potential (approximately between -0.4 and -0.5 V) and the electrode potential was then scanned toward less negative values. Oxidation currents above -0.20 V could be tentatively related to the

oxidation of adsorbed 4-ABT (whose presence will be spectroscopically confirmed below) or, eventually, to the oxidation of the electrode surface (more probable in the case of the silver electrode). The most interesting feature in the subsequent negative-going sweep is a cathodic process which takes place at -0.98 and -0.78 V for Ag and Pt, respectively. This process has been attributed to an electrochemical reductive desorption of the 4-ABT layer which has been adsorbed at higher potentials. This feature explains the hysteresis observed in this potential region. At lower potentials, the reduction current recorded is due to the hydrogen evolution on the electrode surface.

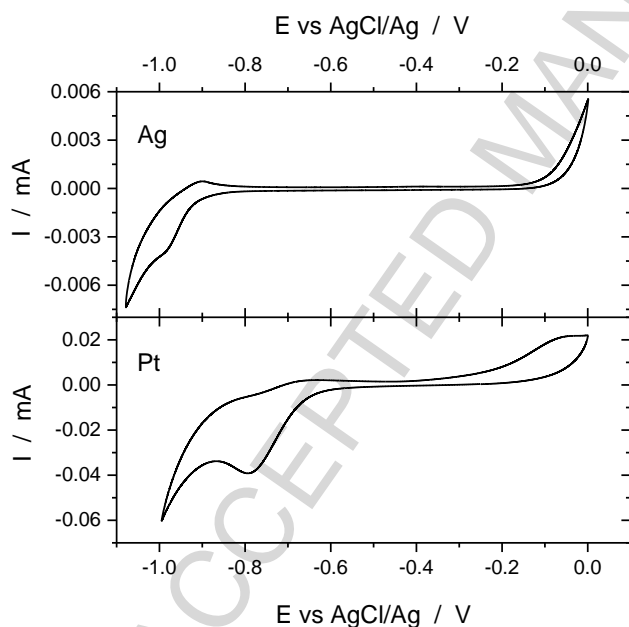


Figure 1. Voltammetric profiles of Ag and Pt massive electrodes in contact with a 0.1 M  $\text{NaClO}_4 + 10^{-3}$  M 4-ABT solution. Sweep rate:  $50 \text{ mVs}^{-1}$ .

In figure 2, lines A and B correspond to the SERS spectra of a self-assembled monolayer of 4-ABT on a silver massive electrode decorated with silver nanoparticles at -0.5 V and -0.9 V, respectively. The used excitation wavelength is 532 nm, but similar results have been obtained with the He-Ne laser as excitation source. For the sake of comparison, the normal Raman spectrum of the solid 4-ABT is also shown (line C). In

addition, in Table 1 the main Raman frequencies of 4-ABT and their assignment, taken from [24] and [29], are summarized.

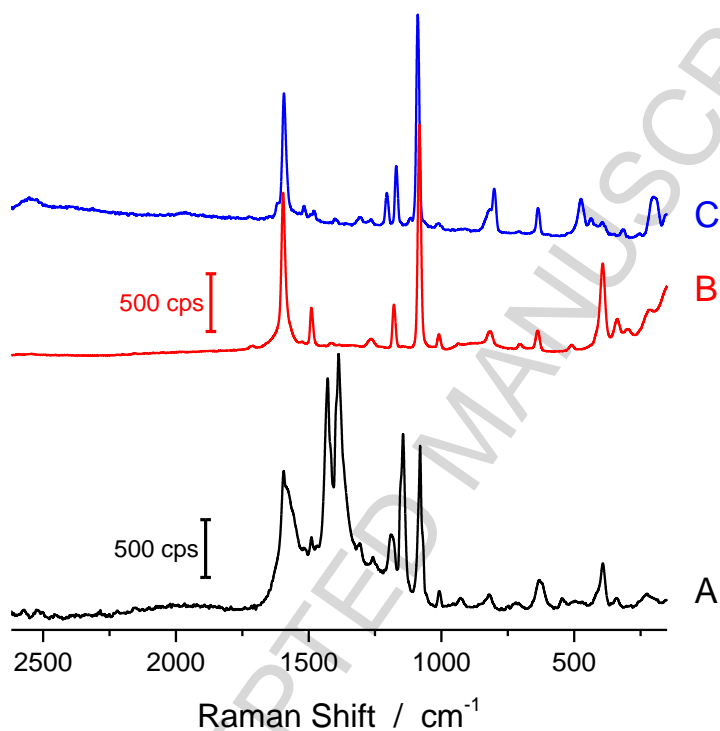


Figure 2. SERS spectra of a self-assembled monolayer of 4-ABT on silver nanoparticles at (A) -0.5 V and (B) -0.9 V vs AgCl/Ag (test solution 0.1 M NaClO<sub>4</sub> + 10<sup>-3</sup> M 4-ABT) and (C) normal Raman spectrum of the solid 4-ABT

Table 1. Raman and main SERS and SEIRA vibrational frequencies of 4-ABT

Raman <sup>(a)</sup>	SERS <sup>(b)</sup>		SEIRA <sup>(b)</sup>	SERS <sup>(c)</sup>		Assignment <sup>[24, 29]</sup>
	-0.9 V	-0.5 V	-0.9 V	-0.9 V	-0.5 V	
200						$\pi$ [CN]+ $\pi$ [CS] + $\tau$ [CC] (b <sub>1</sub> )
	217	217				$\nu$ [Ag-S]
315						$\delta$ [CH]+ $\delta$ [CS] (b <sub>2</sub> )
394	392	392		405	405	$\nu$ [CS]+ $\delta$ [CC] (a <sub>2</sub> )
475						$\gamma$ [CCC] (a <sub>1</sub> )
636						$\gamma$ [CCC] (a <sub>1</sub> )
801						$\nu$ [CH]+ $\nu$ [CS]+ $\nu$ [CC] (a <sub>1</sub> )

820						$\pi[\text{CH}]$	(b <sub>1</sub> )
1010	1009	1009	1010	1007	1007	$\gamma[\text{CC}]+\gamma[\text{CCC}]$	(a <sub>1</sub> )
1089	1083	1080	1083	1078	1078	$\nu[\text{CS}]$	(a <sub>1</sub> )
1118						$\delta[\text{CH}]$	(b <sub>2</sub> )
		1144			1146	$\delta[\text{CH}]$	(b <sub>2</sub> )
1170	1178	1187	1178	1177	1177	$\delta[\text{CH}]$	(a <sub>1</sub> )
1206						$\delta[\text{CH}]$	(a <sub>1</sub> )
1263			1259			$\delta[\text{CH}]$	(a <sub>1</sub> )
1307						$\nu[\text{CC}]+\delta[\text{CH}]$	(b <sub>2</sub> )
		1388			1385	$\nu[\text{CC}]+\delta[\text{CH}]$	(b <sub>2</sub> )
		1429			1436	$\nu[\text{CC}]+\delta[\text{CH}]$	(b <sub>2</sub> )
1479	1490	1490	1488	1487	1487	$\nu[\text{CC}]+\delta[\text{CH}]$	(a <sub>1</sub> )
		1573			1573	$\nu[\text{CC}]$	(b <sub>2</sub> )
1593	1597	1597	1596	1589	1587	$\nu[\text{CC}]$	(a <sub>1</sub> )
1616			1625			$\delta[\text{NH}]$	
2550						$\nu[\text{SH}]$	

- (a) Solid  
 (b) Adsorbed on Ag surface  
 (c) Adsorbed on Pt surface

In the case of silver, the medium-strong bands in the normal Raman at 200 (b<sub>1</sub>), 475 (a<sub>1</sub>), 801 (a<sub>1</sub>) and 1206 (a<sub>1</sub>) cm<sup>-1</sup> are missing in the spectrum obtained at -0.9 V (figure 2, line B) whereas new bands at 392 (a<sub>2</sub>) and 1490 (a<sub>1</sub>) cm<sup>-1</sup> appear. In addition, the band at 1010 (a<sub>1</sub>) cm<sup>-1</sup> is markedly enhanced. Furthermore, the medium-strong band at 1170 (a<sub>1</sub>) cm<sup>-1</sup> shifts to 1178 (a<sub>1</sub>) cm<sup>-1</sup> and the very-strong bands at 1089 (a<sub>1</sub>) and 1593 (a<sub>1</sub>) cm<sup>-1</sup> shift in opposite directions to 1083 and 1597 cm<sup>-1</sup> but keeping the ratio of their intensities. Finally, a new band at 217 cm<sup>-1</sup> assignable to the Ag-S stretching [24] appears in the spectra A and B (monolayer adsorbed) whereas the weak band at 2550 cm<sup>-1</sup> observed in spectrum C corresponding to the stretching of the S-H bond is missing. This fact indicates that the S-H bond is broken in the adsorption process and the 4-ABT is adsorbed onto the silver surface through the sulphur atom. On the other hand, as it has been previously reported [24, 26, 27], when the electrode potential moves from -0.9 V to -0.5 V the recorded SERS spectrum is significantly different. Thus, four new bands are visible at 1144 (b<sub>2</sub>), 1388 (b<sub>2</sub>), 1429 (b<sub>2</sub>) cm<sup>-1</sup> and 1573 (b<sub>2</sub>) cm<sup>-1</sup> (this later as a broad shoulder). Note, that the latter notation is based on the assignments done by [24] (see table 1), who ascribed these bands to ring vibrations of

the adsorbed 4-ABT molecule. However, these bands are assigned to different vibrational modes of 4,4'-DMBA [27] (see discussion below).

As previously discussed in the introduction section, platinum is intrinsically a weak SERS substrate because, on this metal, the efficient excitation of surface plasmon is difficult [7-10]. In order to circumvent this limitation, different strategies have been used to obtain SERS information always with the aim of preparing a surface with a certain roughness or an appropriate morphology. Examples of these methods are the electrochemically activation of the surface (oxidation-reduction cycling [11]), the use nanoparticles deposited on a substrate, the so-called nanoparticles-on-electrode approach [12], or the Kim approach [31] among others. Interestingly, our experimental results obtained for silver at -0.5 V (Fig. 2A) by the nanoparticles-on-electrode approach [12] agree with the SERS spectra obtained by Kim [31] after attaching Ag nanoparticles to the amine groups of 4-ABT adsorbed on smooth Pt [31].

Figure 3 shows the SERS spectra obtained at -0.90 V for 4-ABT adsorbed on Pt nanoparticles (spectrum A) and silver (spectrum B). It can be seen that similar features appear in both spectra (see also Table 1 and ref. [24] for 4-ABT adsorbed of silver), although the two strong bands shift slightly to the red in the case of platinum, at 1078 and 1589  $\text{cm}^{-1}$ , and their intensities are similar, whereas the medium-strong low frequency band moves to the blue, at 405  $\text{cm}^{-1}$ . Again, as observed with the silver nanoparticles, new bands appear at 1146, 1385 and 1436  $\text{cm}^{-1}$  when the electrode potential moves from -0.9 V to -0.5 V. A fourth band, about 1583  $\text{cm}^{-1}$ , overlaps with that appearing at 1589  $\text{cm}^{-1}$  at -0.90 V (figure 4).

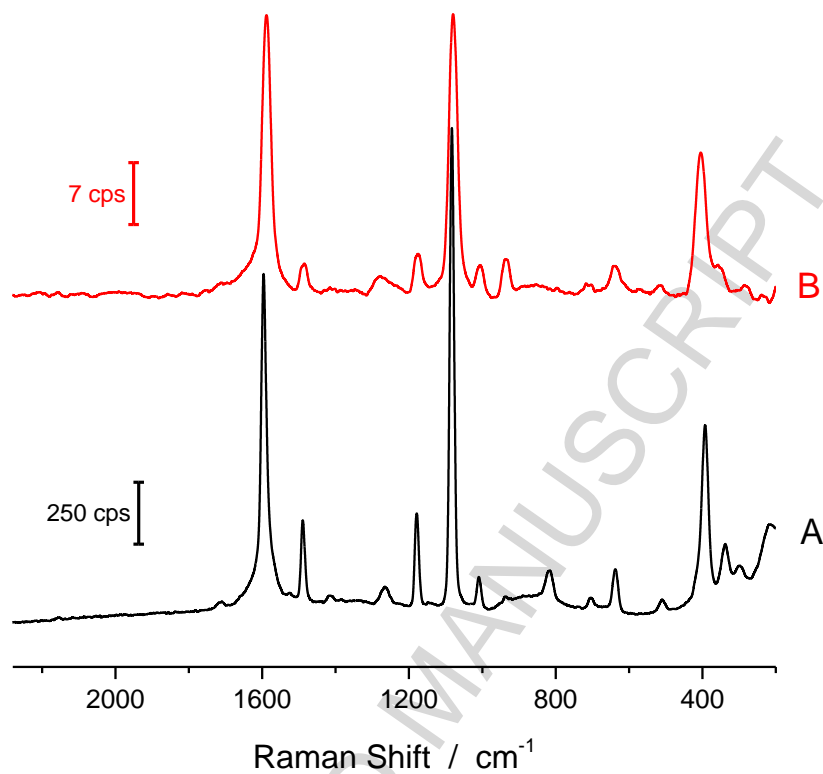


Figure 3. SERS spectra of a self-assembled monolayer of 4-ABT on silver (A) and platinum (B) nanoparticles at  $-0.9$  V vs AgCl/Ag. Test solution  $0.1$  M  $\text{NaClO}_4$  +  $10^{-3}$  M 4-ABT.

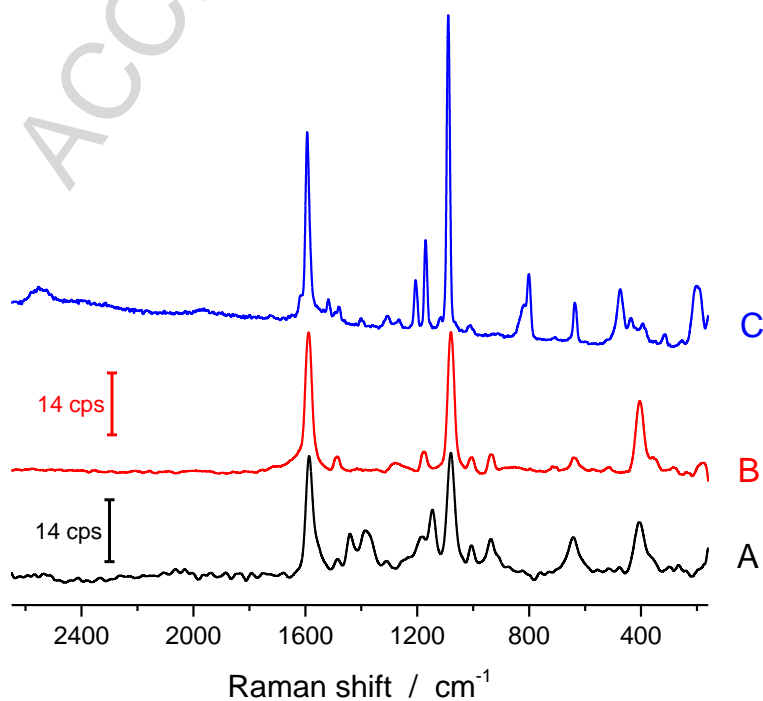


Figure 4. SERS spectra of a self-assembled monolayer of 4-ABT on platinum nanoparticles at (A) -0.5 V and (B) -0.9 V vs AgCl/Ag (test solution 0.1 M NaClO<sub>4</sub> + 10<sup>-3</sup> M 4-ABT) and (C) normal Raman spectrum of the solid 4-ABT.

On the other hand, it has been reported that the power density of the laser employed in the SERS measurements has a great influence and may induce the formation of new compounds [26]. To evaluate this particular effect, two different sets of spectra have been obtained working at the same potentials for the same substrate but changing the power density of the applied laser. In more detail, we have changed the incident power density by defocusing the laser beam on the substrate and opening, at the same time, the confocal aperture. Spectra obtained in the case of silver (A, B) and platinum (C, D) nanoparticles are reported in Figure 5. When the power density is low (about 10<sup>2</sup> mWcm<sup>-2</sup>) the SERS spectra for 4-ABT adsorbed on platinum are dominated by the bands at 1007, 1078, 1177, 1487 and 1588 cm<sup>-1</sup> attributed to a<sub>1</sub> modes of 4-ABT, together with the a<sub>2</sub> band at 405 cm<sup>-1</sup>. No bands related to non-a<sub>1</sub>-type modes are observed irrespective of the electrode potential. Nevertheless, when a higher power density (about 10<sup>7</sup> mWcm<sup>-2</sup>) is used without changing the sampling position, three new bands appear at 1146, 1385 and 1436 cm<sup>-1</sup> in the spectra collected for potentials above -0.50 V. In addition, the band about 1588 cm<sup>-1</sup> becomes broader and can be deconvoluted into two bands at 1583 (b<sub>2</sub>) and 1587 (a<sub>1</sub>) cm<sup>-1</sup>. All four bands can be assigned to non-a<sub>1</sub>-type symmetry species. Interestingly, if the potential is shifted to values below -0.60 V (where a cathodic current is observed in the voltammogram (figure 1)) these bands disappear. A similar behaviour is observed in Figure 5 for 4-ABT adsorbed on silver. In this regard, it is worth noting that similar bands were also

observed in other comparable systems such as 4-ABT and p-nitrothiophenol (4-NBT) on Cu<sub>2</sub>O nanoparticles [40].

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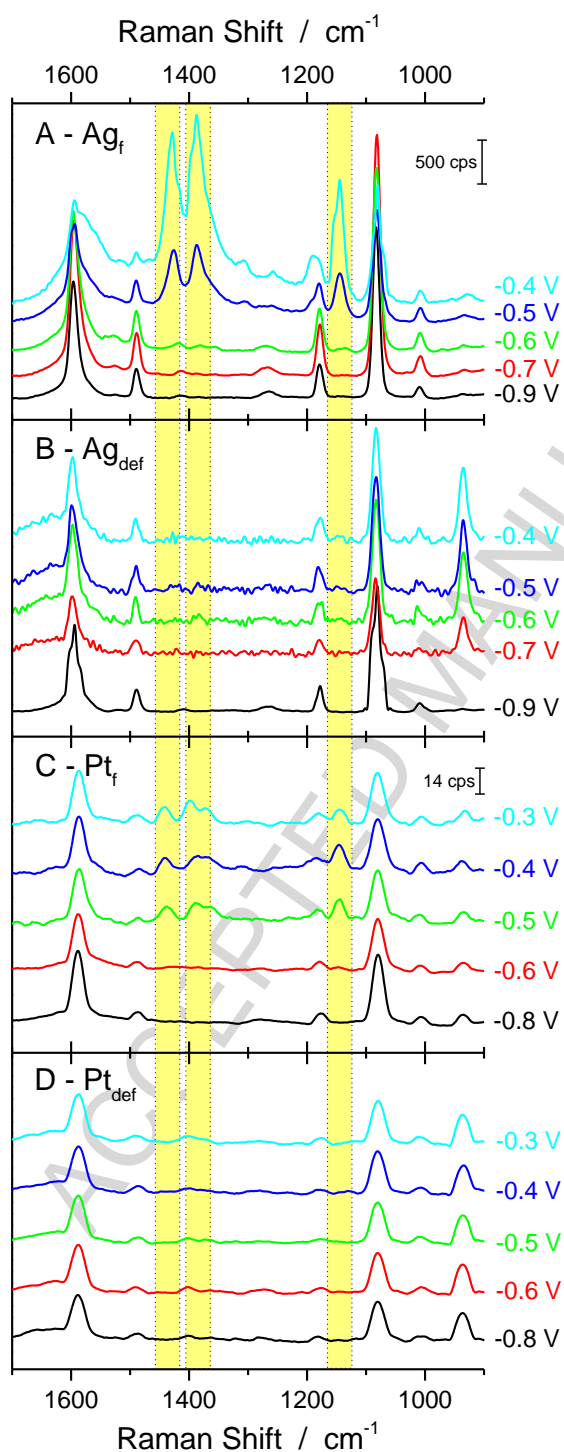


Figure 5. SERS spectra recorded at different electrode potentials for a self-assembled monolayer of 4-ABT on (A and B) silver and (C and D) platinum nanoparticles focused (A and C) and defocused (B, 300  $\mu\text{m}$ , and D, 40  $\mu\text{m}$ ) at the electrode surface. Test solution 0.1 M  $\text{NaClO}_4$  +  $10^{-3}$  M 4-ABT.

Finally, in order to evaluate the behaviour of the isolated aggregates of Pt nanoparticles and avoid any possible contribution from the Pt support, we have decorated a glassy carbon electrode with the Pt nanoparticles which have been employed as SERS substrate for the adsorption of 4-ABT. The set of spectra observed (not shown) follows the same pattern as those obtained with the Pt electrode decorated with the same Pt nanoparticles (figure 5). Thus, when the electrode potential is set at  $-0.9$  V several bands are obtained at  $1009$ ,  $1083$ ,  $1178$ ,  $1485$  and  $1594$   $\text{cm}^{-1}$  attributed to  $a_1$  modes of 4-ABT, beside the D-band of carbon at  $1330$   $\text{cm}^{-1}$ . Nevertheless, at  $-0.3$  V, three new bands are clearly visible at  $1144$ ,  $1387$  (as a shoulder in the D-band of the carbon) and  $1427$   $\text{cm}^{-1}$  all of them non- $a_1$ -type. At this time, an interesting question about whether or not the time between acquisitions of spectra could have some influence comes up. In this regard, Figure 6 shows three spectra obtained at the same surface position and with a power density of about  $10^7$   $\text{mWcm}^{-2}$ . First, a spectrum at  $-0.9$  V was obtained (spectrum A in figure 6). Then, the laser was shut off and the electrode potential was changed to  $-0.3$  V where, according with the SEIRA spectra of 4-ABT adsorbed onto a silver film (see later, figure 7), no new species should be formed only by pure electrochemical means in this range of potentials. After four minutes at this potential, the laser was once again opened and a spectrum was immediately recorded in a few seconds (spectrum B in figure 6). Interestingly, and in spite of the fact that the electrode potential was maintained at  $-0.3$  V for four minutes (with the laser shut off), the differences between these two spectra (6A) and (6B) are hardly noticeable, but spectra (6B) and (6C) show clear differences. However, if we hold the potential with the laser on for one minute and then a new spectrum is recorded at the same position (spectrum C in figure 6), the presence of non- $a_1$ -type bands is now clearly observed. These results suggest that these non- $a_1$ -type bands come from new

species formed by a photochemical process of the adsorbed 4-ABT. This experimental evidence seems to be in agreement with Tian's group [26, 27] who claimed that the non- $a_1$ -type bands would correspond to N=N stretching vibrations of 4,4'-dimercaptoazobenzene (4,4'-DMAB) produced from 4-ABT via a photocatalytic coupling reaction (according to the spectral similarity of 4-ABT and 4,4'-DMAB). Therefore, the proposal of a contribution of the CT mechanism of enhancement as a consequence of the alteration of electronic states of benzenethiol by the introduction of an  $\text{NH}_2$  group on the benzene ring [24, 25] cannot only explain, in our opinion, the time dependence observed.

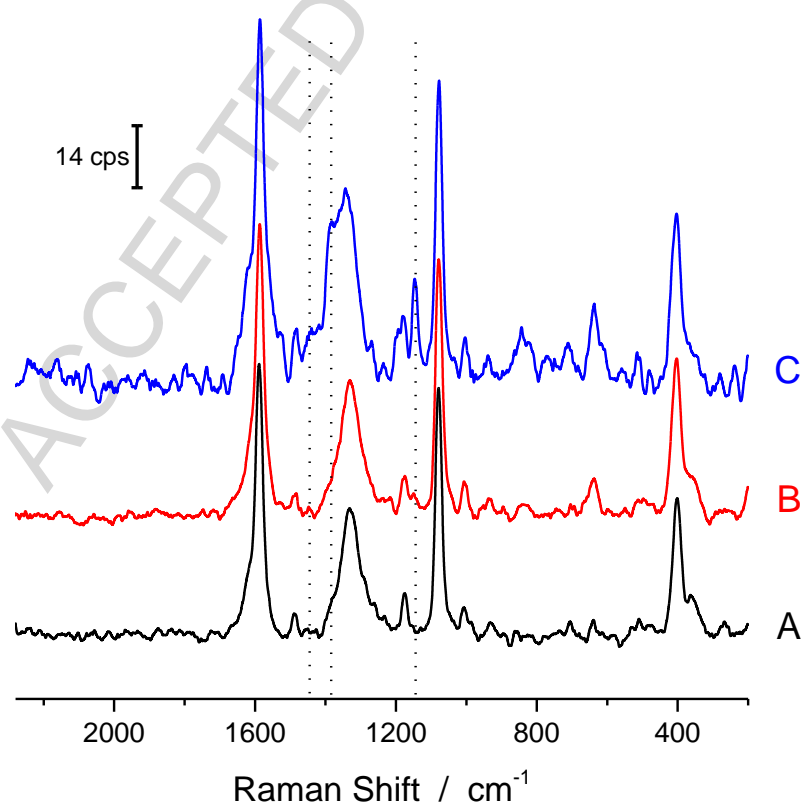


Figure 6. SERS spectra recorded at the same position of a self-assembled monolayer of 4-ABT on PtNP deposited onto a glassy carbon at (A) -0.9, (B) -0.3 (after keeping that potential for four minutes with the laser shut off) and (C) -0.3 V after another minute at

that potential with the laser on. Test solution 0.1 M NaClO<sub>4</sub> + 10<sup>-3</sup> M 4-ABT. Dotted lines indicate the non-a<sub>1</sub>-type bands. The feature at 1330 cm<sup>-1</sup> corresponds to the D-band of the carbon substrate.

### 3.2 SEIRAS study

Taking into account the existence of the redox processes shown in the cyclic voltammetry of the 4-ABT reported in figure 1, it is interesting to check whether the electrode potential alone can give rise to some of the characteristics features observed in the SERS spectra of the adsorbed molecule reported in Figures 2 to 5. This can be done by analyzing the potential-dependent behaviour of the infrared spectra of adsorbed 4-ABT, i.e. under conditions where no laser is used. This kind of experiment is facilitated by the surface-enhanced absorption that takes place when the probe molecule is adsorbed on a metal thin film (the so-called SEIRA effect [41, 42]). Higher enhancements and easier preparation conditions for the silver thin films when compared to platinum, has prompted us to choose the former metal to carry out the SEIRAS experiments to obtain the potential-dependent infrared spectra of adsorbed 4-ABT. These experiments were performed under attenuated total reflection conditions (Kretschmann's configuration [41]) with a silver thin film chemically deposited onto a germanium substrate [33]. The obtained SEIRA spectra, which are reported in Figure 7, are referred to the single beam spectrum collected at -1.0 V before dosing 4-ABT to the sodium perchlorate test solution. Thus, infrared bands related to adsorbed 4-ABT (as well as those for any other species not being present when collecting the reference spectrum) are expected to appear as positive-going features. The SEIRA spectrum collected at -1.0 V after dosing 4-ABT shows several bands at 1010, 1083, 1178, 1259, 1488 and 1596 cm<sup>-1</sup> which also appear in the SERS spectrum of 4-ABT at this electrode potential (see table 1). A weak band at 1625 cm<sup>-1</sup> could be tentatively assigned to the

$\delta[\text{NH}]$  [24] of the amine group in the adsorbate. However, some contribution to this feature from the uncompensated (O-H) bending mode of interfacial water can be also expected. Since non- $a_1$ -type modes are missing in the SEIRA spectra, their assignment to ring vibrations of the 4-ABT molecules would imply that the latter must be adsorbed normally to the surface. Main changes observed in the spectra collected at -1.0 V when the electrode potential is stepped to increasingly higher potentials up to 0 V are related to a) an increase of the intensity of the band at  $1625\text{ cm}^{-1}$  described above, b) the observation of a small feature at ca.  $1200\text{ cm}^{-1}$  (also observed in the Raman spectrum of solid 4-ABT (see table 1) but hardly visible in the SEIRA spectrum collected at -1.0 V), c) the upward shift and broadening of the band initially at  $1259\text{ cm}^{-1}$  and d) the development of a strong absorption band at ca.  $1100\text{ cm}^{-1}$ . This feature, which is observed with a similar potential-dependent behaviour in the SEIRA spectra collected for the silver thin film electrode in the 4-ABT-free sodium perchlorate solution, can be related to the presence of co-adsorbed perchlorate anions whose surface coverage would increase as the electrode potential increase. In the same way, the increasing intensity of the band at  $1625\text{ cm}^{-1}$  in Figure 6 could be related to the coadsorption of interfacial water molecules associated to the perchlorate anions. In any case, it is clear from the spectra reported in Figure 6 that none of the bands appearing in the SERS spectrum collected at potentials equal or higher than -0.50 V for 4-ABT adsorbed on silver (spectrum A in Figure 2) appears in the SEIRA spectra collected for the silver electrode in the presence of 4-ABT in a similar potential range.

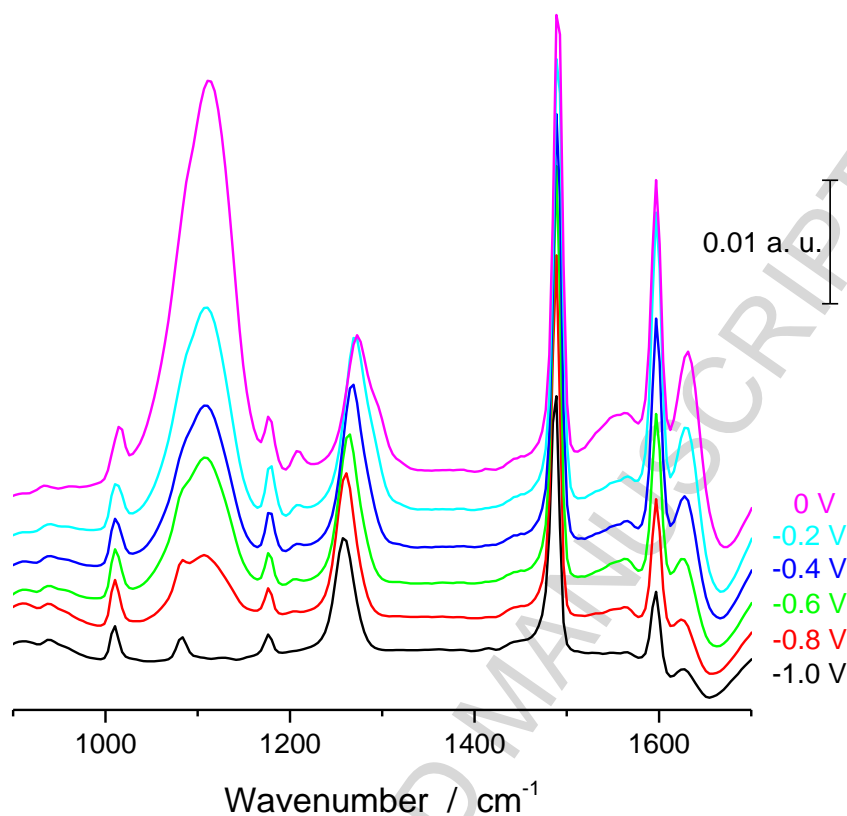


Figure 7. SEIRA spectra of 4-ABT adsorbed onto a silver film recorded at different electrode potentials. Test solution: 0.1 M NaClO<sub>4</sub> + 10<sup>-3</sup> M 4-ABT. The reference spectrum was collected at -1.0 V before the dosing of 4-ABT.

#### 4. Conclusions

We have studied the adsorption of 4-ABT on Ag and Pt substrates by spectroelectrochemical means. Similar SERS spectra were obtained when 4-ABT is adsorbed on Ag and Pt. Interestingly, new species are progressively observed in the SERS spectrum when the potential range is more positive than -0.6 V which disappear if the potential is shifted to more negative values. The particular effect of power density of the laser employed in the SERS measurement has been also evaluated. These new species seem to be related to a photochemical process of the 4-ABT which is clearly

affected by the energy density of the laser (defocusing experiments) and could give rise to the formation of 4,4'-dimercaptoazobenzene (4,4'-DMAB). On the other hand, from the SEIRA spectra of 4-ABT adsorbed onto a silver film recorded at different electrode potentials, we have concluded that no new species were formed only under electrochemical control. In this way, the voltammetric reduction currents observed below -0.98 and -0.78 V for Ag and Pt, respectively, in the absence of laser irradiation do not seem to be related to the reduction of 4,4'-DMAB. Additional time dependent experiment supports the occurrence of a photochemical process. The participation of a possible CT enhancement as a consequence of the alteration of the electronic states of benzenethiol by the introduction of an NH<sub>2</sub> group on the benzene ring should not be the main responsible of the appearance of the new SERS bands.

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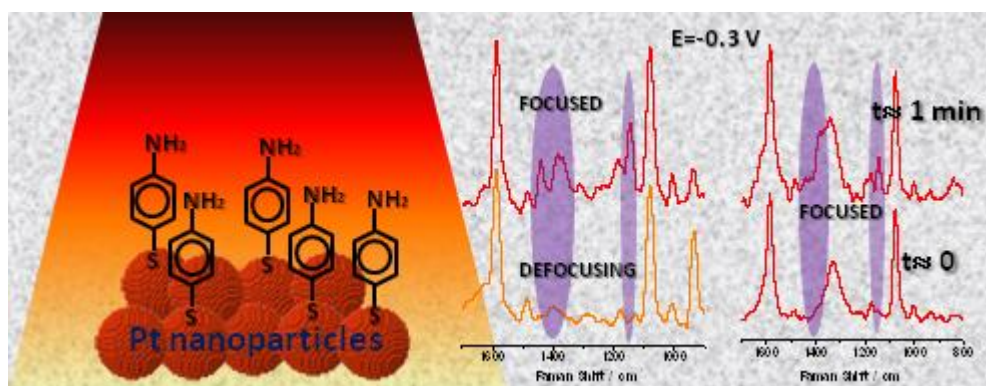


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Graphical abstract

### Highlights

- The adsorption of 4-ABT on Ag and Pt by spectroelectrochemical means is studied
- No new species are formed only by electrochemical means as suggested by SEIRAS
- SERS spectra are dependent on the laser power density and the electrode potential
- SERS spectra show a strong time dependence

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