The adsorption and orientation of pyrazine on silver electrodes: a surface enhanced Raman scattering study

Alexandre G. Brolo, Donald E. Irish *

Guelph Waterloo Centre for Graduate Work in Chemistry, Department of Chemistry, University of Waterloo, Waterloo, Ont. N2L 3G1, Canada

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Abstract

Surface enhanced Raman scattering (SERS) spectra of pyrazine (pz) adsorbed on a silver electrode from aqueous solutions containing either 1.0 M KCl or 1.0 M KBr are presented. The SER spectra display bands which are usually forbidden in the normal Raman spectrum of pz. The presence of these forbidden bands and the orientation of the molecules on the electrode surface are discussed under the two most accepted surface enhancement theories: the charge transfer and the electromagnetic model. The dependence of SERS intensity of several pz vibrational modes on the applied potential (potential profile) is also presented for different pz concentrations and excitation wavelengths. SER spectra, obtained at potentials more negative than —900 mV (vs. SCE), contain new bands due to reduction of the pz molecule. It is clear that some of these products of decomposed pz remain trapped on the electrode surface, and this can lead to misunderstandings of the interpretation of the adsorbed pz spectrum. Several controversial aspects presented in the literature about the surface Raman spectrum of pz are clarified and discussed.

Keywords: Surface enhanced Raman scattering; Pyrazine; Silver; Adsorption; Orientation; Enhancement theories

1. Introduction

Surface enhanced Raman spectroscopy (SERS) is a very powerful technique for the study of adsorption of molecules on metallic surfaces. Earlier controversies about the enhancement mechanism have diminished. There is general consensus that both the electromagnetic and chemical enhancement mechanisms contribute to the overall effect; the predominant mechanism will depend on the nature of the system and on the experimental conditions. However, some fundamental aspects of SERS, including the relation between SER intensity and both surface coverage and molecular orientation, require further investigation.

An extensive study concerning the relationship between SER intensity and surface coverage involving the adsorption of pyridine on gold electrodes has been conducted [1,2]. A linear relationship was found between the SER intensity and the surface coverage to about 60% of a monolayer for a 'smooth' electrode. Extension of this work would involve the SERS study of other molecules, such as pyrazine, on the electrode surface. Preliminary results of the SER spectra of pyrazine (pz) on a gold electrode have been obtained [3]. Progress in understanding the relationship between the SERS intensity of pz and surface coverage is dependent on knowledge of the molecular orientation, and consequently, of the origin of all bands. We have recently identified and assigned all Raman bands of pz and its protonated forms [4].

The relationship between the vibrational mode activity and band intensity with molecular orientation can be inferred from the application of the SERS selection rules. These can be derived from both the charge transfer (CT) and electromagnetic model (EM) enhancement mechanisms [5]. Pz adsorption on a metallic surface is a good system to test the application of SERS selection rules derived from these two models.

Several studies of the adsorption and/or application of the SERS selection rules involving pz on metals have been reported [6–13]. However, the literature has revealed several controversial aspects. Differences in the spectral features reported by different workers need to be resolved. The objective of our work is to rationalize these SERS results of pz adsorbed on silver electrodes. Some of the unusual bands and controversial conclusions obtained in the previous works will be discussed. Assignments for the surface enhanced pz bands will also be reviewed.

* Corresponding author.
2. Experimental

2.1. Reagents

The following chemicals were used without further purification: \( \text{pz} \) 99 + % from Aldrich, KBr and KCl AnalR grade from BDH. All solutions were prepared with Milli-Q-water.

2.2. Electrochemistry

The three-electrode spectroelectrochemical cell has been described elsewhere [14]. A PAR model 273 potentiostat was used to control the applied potential of the working electrode. The counter electrode was a 0.3 mm platinum wire (99.9%). A saturated calomel electrode (SCE) was used as reference. The working electrode was made from 99.9% polycrystalline silver rod. A silver disk of ca. 2 mm radius was mounted in a Teflon holder. The working electrode was first polished with emery paper, and then with progressively finer grades of alumina powder down to 0.3 \( \mu \text{m} \). The electrode was rinsed with an abundant amount of Milli-Q-water, sonicated, rinsed again, and transferred to the spectroelectrochemical cell. The solution was degassed with Ar for 30 min prior to the experiment, and a gentle stream of Ar was kept on during data acquisition.

2.3. Activation procedures

The process of roughening the metal surface electrochemically, in order to create the necessary SERS active

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**Fig. 1.** Region 1 spectrum: activation in the presence of \( \text{pz} \). Regions 2, 3 and 3A spectra: activation in the absence of \( \text{pz} \). (a) 1.0 M aqueous pyrazine solution. (b) 1.0 M aqueous pyrazine in 3.0 M HCl solution. The spectral features are due to the monoprotonated \( \text{pz} \) cation, \( \text{pzH}^+ \). (c) SER spectrum of \( \text{pz} \) on a silver electrode from 1.0 M KBr + 0.1 M \( \text{pz} \) solution. \( E = -600 \text{ mV} \). Region 3A is an enlarged version of region 3. The schematic representation of \( \text{pz} \)'s vibrational modes (from Ref. [15]) is also presented. The Wilson numbering scheme is given within each representation. The number underneath each representation is the SER vibrational frequency in wavenumbers.
sites, is called the activation procedure. In this work, two
distinct activation procedures were used.

In the first, oxidation–reduction cycles (ORCs) were
performed on the silver electrode immersed in an aqueous
solution containing 1.0 M halide and the desired pz
concentration. The scan rate was 5 mVs⁻¹ and the laser light
was illuminating the surface during the cycles. The well-
known time dependence of the SER spectrum when the
electrode is activated this way was avoided by performing
an ORC and stopping at the desired potential before each
acquisition. This procedure gives reproducible and time-in-
dependent spectra [1]. This method will be referred to in
the text as “activation in the presence of pz”.

The second activation procedure consisted of applying
several ORCs to the silver electrode in an aqueous solution
containing 1.0 M halide, the other conditions being the
same as above. Then, the potential immediately after the
silver ion reduction was held, and pz was added to the
system using a syringe. This procedure yields weaker
SERS signals; however, it avoids the activation of bands
due to trapped pz or from pz decomposition products, and
the SER spectrum is also time independent. This procedure
will be referred to as “activation in the absence of pz”.

2.4. Raman spectra

Raman spectra were measured with a Dilor OMARS 89
spectrometer with an optical multichannel analyser. The
intensified diode array (512 diodes) detector was thermo-
electrically cooled to ca. −10°C. The spectrometer was
interfaced to an IBM PC-AT computer. Data were trans-
ferred to an IBM 486 computer on which baseline correc-
tion, band-fitting, and plotting programs were available.
Spectra were excited by the 514.5 nm (100 mW at the
head) line from a Coherent Innova 70 argon ion laser,
chopped at a 1 s cycle, as required by the Dilor spectrome-
ter.

3. Results and discussion

This section is divided into five parts. In Section 3.1 the
general features of the SER spectrum and its potential
dependence are discussed. Section 3.2 gives some general
background on the SER selection rules, which are used in
the discussion of pz’s molecular orientation, presented in
Section 3.3. The electrochemical reduction of pz in a
halide medium is discussed in Section 3.4, and a compari-
sion of the present data with previous results presented in
the literature is given in Section 3.5.

3.1. SERS of pz and its dependence on the applied potential

In Fig. 1, regions 1 to 3, the normal Raman spectra
(NRS) of pz and pzH⁺ cation in aqueous solution are
compared with the SERS spectrum of pz on the silver
electrode. For the pzH⁺ cation, the binding of a hydrogen
to one of the nitrogen atoms leads to a symmetry lowering
similar to an end-on adsorption of the pz molecule on an
electrode surface. Spectra of aqueous pz and its protonated
forms have been described elsewhere [4]. The Raman
intensities presented in Fig. 1 are arbitrary, and conve-
niently chosen for a better comparison. Examining those
spectra, one can notice that the peak positions do not shift
very much on adsorption from the values for the aqueous
pz species. However, regarding peak positions, it seems
that the spectrum of adsorbed pz resembles that of the
aqueous pz rather than the aqueous pzH⁺. Adsorption to
the electrode surface relaxes the selection rules for Raman,
and some NRS forbidden bands of aqueous pz become
active. The appearance of forbidden bands is anticipated
by both the electromagnetic and the chemical enhancement
mechanisms [5]. In order to facilitate the following discus-
sion, the schematic representation of some pz vibrational
modes, analogous to the benzene modes presented by Lord
et al. [15], are also displayed in Fig. 1.

The spectra in the low frequency region, Fig. 1, region
1, for aqueous pz species solutions were not shown, be-
cause no bands were observed in that region. In contrast,
two ring deformation modes are observed from the elec-
trode surface: the A₈ ring puckering at ca. 360 cm⁻¹,
which is observed only when the electrode is activated in
the pz’s presence, and the B₂, ring deformation at ca.
430 cm⁻¹. It is important to point out that the ca. 360 cm⁻¹
band is a silent mode even in the IR spectrum, and some
work reports only its estimated or calculated value (e.g.
Ref. [16]). Hence, the relative enhancement of these two
modes is very significant.

In Fig. 1, region 2, the most intense peak of the SER
spectrum is due to the A₈ (6a) ring mode at ca. 630 cm⁻¹.
This band is weak for both the aqueous pz (at 620 cm⁻¹)
and aqueous pzH⁺ solutions (at 606 cm⁻¹). The dominant
band from aqueous solutions in this region is the B₂ (6b)
ing mode, which shows up at 702 cm⁻¹ for the aqueous
pz and 690 cm⁻¹ for the aqueous pzH⁺. This mode gives a
weak feature at ca. 700 cm⁻¹ from the electrode surface.

From the spectra in Fig. 1, region 3 and region 3A, one
can conclude that the relative intensity of the ring-breath-
ing mode decreases substantially on the electrode surface
at −600 mV compared with aqueous pz. For instance,
from the aqueous pz solution the A₈ (1) ring-breathing
mode at 1019 cm⁻¹ is about six times greater than the A₈
(8a) symmetrical in-plane CH bending mode at 1593 cm⁻¹,
and from the aqueous pyrazinium solution the ring-breath-
ing mode at 1020 cm⁻¹ is five times greater than the
in-plane CH bending mode, 1634 cm⁻¹. From the elec-
trode surface, however, both modes have approximately
the same intensity at the given potential. Nevertheless,
it is also important to point out that the relative intensity of
bands in the SERS spectrum is highly potential sensitive.
For instance, the ca. 1590 cm⁻¹ band is stronger than the
1020 cm\(^{-1}\) band at -750 mV in a bromide medium. It is also important to notice that the free \(pz\) \(B_{1u}\) (12) mode, which is Raman forbidden but shows up in the aqueous \(pzH^+\) at 1030 cm\(^{-1}\) as a very strong band, does not appear strongly from the electrode surface; its presence is observed in certain conditions as a weak band at 1040 cm\(^{-1}\).

Two bands are observed, Fig. 1, region 3A, in the electrode surface spectrum at 1215 cm\(^{-1}\) and 1235 cm\(^{-1}\). The former band was assigned as a combination (11 + 16b), and the latter to the fundamental 9a 5CH \[4\). These two bands are similar in frequency to those observed in the aqueous \(pz\) spectrum, but they are better resolved in the spectrum of \(pz\) adsorbed on the electrode surface. The high intensity presented by this combination band can be attributed to a Fermi resonance phenomenon, because both the fundamental and the combination mode have the same symmetry (\(A_2\)) and similar frequencies. All the frequencies of the bands observed from the electrode surface are summarized in Table 1.

Fig. 2, regions 1 and 2, show spectra of \(pz\) adsorbed from 1.0 M KCl solutions to the silver electrode at several potentials. The spectra presented in Fig. 2 were obtained after an activation procedure in the absence of \(pz\); however, the overall features of these spectra do not change for the different surface preparations (activation procedures), although the bands obtained after ORC in the presence of \(pz\) are more intense than those obtained by electrode activation in the supporting electrolyte and subsequent addition of \(pz\). The only band which shows up in the former treatment and not in the latter is the weak 360 cm\(^{-1}\) band.

For a given excitation energy, the potential \(E_{\text{max}}\) where the spectral intensities maximize is dependent on the activation procedure, on the halide nature, and on the halide concentration. Generally, \(E_{\text{max}}\) is 50 mV more negative when the electrode is activated in the presence of \(pz\). Typically, \(E_{\text{max}}\) values obtained when the electrode is activated in the presence of \(pz\) range between ca. -750 and -800 mV for 1.0 M KBr and from ca. -550 to -600 mV for 1.0 M KCl.

Broad envelopes, containing at least two bands, are observed at ca. 240 cm\(^{-1}\) in a chloride medium (Fig. 2, region 1) and at ca. 150 cm\(^{-1}\) in a bromide medium. These bands are assigned as metal–halide stretch vibrations, and

<table>
<thead>
<tr>
<th>Assignment</th>
<th>(\bar{v} / \text{cm}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A_2) (16a)</td>
<td>360 (vw)</td>
</tr>
<tr>
<td>(B_{2u}) (16b)</td>
<td>432 (w)</td>
</tr>
<tr>
<td>(A_2) (6a)</td>
<td>630 (m)</td>
</tr>
<tr>
<td>(B_{2g}) (6b)</td>
<td>697 (w)</td>
</tr>
<tr>
<td>(B_{2g}) (4)</td>
<td>741 (w)</td>
</tr>
<tr>
<td>(B_{2u}) (11)</td>
<td>797 (w)</td>
</tr>
<tr>
<td>(B_{1g}) (10a)</td>
<td>916 (vw)</td>
</tr>
<tr>
<td>(A_1) (1)</td>
<td>1019 (s)</td>
</tr>
<tr>
<td>(B_{1u}) (12)</td>
<td>1040 (vw)</td>
</tr>
<tr>
<td>(B_{2u}) (18a)</td>
<td>1116 (vw)</td>
</tr>
<tr>
<td>(A_1) (11 + 16b)</td>
<td>1215 (m)</td>
</tr>
<tr>
<td>(A_2) (9a)</td>
<td>1235 (s)</td>
</tr>
<tr>
<td>(B_{2g}) (3)</td>
<td>1324 (vw)</td>
</tr>
<tr>
<td>(B_{2g}) (8b)</td>
<td>1514 (w)</td>
</tr>
<tr>
<td>(A_2) (8a)</td>
<td>1587 (s)</td>
</tr>
<tr>
<td>(B_{2g}) (7b)</td>
<td>3020 (m)</td>
</tr>
<tr>
<td>(A_2) (2)</td>
<td>3030 (s)</td>
</tr>
</tbody>
</table>

\(^a\) Intensities: v-very; w-weak; s-strong and m-medium. \(^b\) SERS of \(pz\) on silver electrode from halide medium. \(^c\) Relative intensity in parentheses. \(^d\) SERS of \(pz\) on silver colloid. \(^e\) SERS of \(pz\) on coldly deposited silver. \(^f\) NRS of \(pz\) on silver. \(^g\) Possible bands due to trapped \(pz\) or decomposed \(pz\) species (see text).
they are also potential dependent. The presence of multiple bands in the metal–halide region has been reported before [17]. These bands suggest different ‘types’ of silver–halide vibration, and were interpreted as an indication of distinct ‘active sites’ or silver–halide clusters at the rough surface [18]. The intensities of these Ag–halide bands decrease as the potential becomes negative, and they are rather weak at the potential where pz bands maximize. In the potential range where SER bands can be observed for both the pz and the halide, it is quite clear that they are coadsorbed on the electrode surface.

The dependence of the ca. 1020 cm⁻¹ pz band intensity from the ring-breathing mode on the potential for three pz concentrations in 1.0 M chloride medium is presented in Fig. 3. From the analysis of this figure, one can claim that the \( E_{\text{max}} \) moves slightly to more positive values as the pz concentration increases; however, the shift in the \( E_{\text{max}} \) presented there is within the experimental uncertainty. The pz concentration also affects the half-width of the potential profiles. For instance, the half-width values range from ca. 40 mV for 0.0125 M pz to ca. 300 mV for 0.075 M pz in a 1.0 M KCl medium. The dependence of band intensities on applied potential for some important bands in the same spectrum is compared in Fig. 4. It can be noticed that all bands of adsorbed pz maximize at the same potential, close to the potential of zero charge (pzC). Fig. 5 presents potential profiles for pz in a bromide medium at two distinct excitation wavelengths. Again the profiles are wavelength independent.

The SERS results have been interpreted in the literature in terms of the two most accepted theories for the enhancement: the CT mechanism and the EM. In the CT model,

![SERS spectra](image)

**Fig. 2.** Spectra of pz adsorbed on a silver electrode at designated potentials. 1.0 M KCl + 0.1 M pz solution. Activation procedure in the absence of pz. The spectra at low frequencies (region 1) are presented after subtraction of the Rayleigh wing. Region 1: (a) – 200 mV; (b) – 600 mV; (c) – 800 mV. Region 2: (a) – 200 mV; (b) – 400 mV; (c) – 500 mV; (d) – 600 mV; (e) – 700 mV.
the Raman signal enhancement occurs due to a resonance involving the incident radiation and a CT transition between the Fermi level of the metal and the frontier orbitals from the adsorbed molecule. The EM mechanism takes into account the enhancement on the local electromagnetic field induced by the coupling of the incident light with the local resonances present on the metallic surface known as the surface plasmons (SP). The main predictions from these two theories are summarized in Table 2. A recent and comprehensive discussion of the general features from these models can be found elsewhere [19]. Both mechanisms contribute to the overall enhancement, which makes it difficult to quantify the individual contributions from each model, unless one deals with a situation where one of them is very predominant over the other. Being so, considerations from both mechanisms will be taken into account in the following discussion about the SER results presented in this work.

A common feature which can be observed on the potential profiles presented on Figs. 3–5, is the ‘bell-shaped’ pz’s SER intensities vs. potential curves. The EM mechanism predicts that the enhancement should be potential independent, and thus the intensity changes with potential would be due to the variation of surface coverage. In fact, the surface coverage vs. electrode potential plot for a neutral organic molecule is expected to be ‘bell-shaped’, with a maximum around the pz [20]; moreover, the half widths of these plots are expected to increase and their maxima shift slightly to positive potentials with the increase of the adsorbent concentration [20]. All these predictions agree with Fig. 3. However, one must be reminded that a linear relationship between SER intensity and the amount adsorbed does not hold for higher surface coverage values [1,2]. The differences in the $E_{\text{max}}$ obtained for distinct halide media can also be understood using the EM arguments. Supposing that in the absence of specific adsorption the electrode charge would be $\sigma_{\text{m}}^\circ$. In the presence of specifically adsorbed halide, the negative charges at the surface induce a positive counter charge in the polarizable electrode and the electrode charge shifts to a more positive value $\sigma_{\text{m}}$. In other words, the electrode’s pz shifts to more negative potentials. This can explain the reason for the shift of the maximum in the potential profiles ($E_{\text{max}}$) to negative values with the replacement of Cl$^-$ by Br$^-$; thus, bromide ions adsorb more strongly to the surface than chloride ions. The CT mechanism also predicts a symmetric ‘bell-shaped’ curve for the potential profile [21]. In this case, the potential changes would tune the CT process in and off the resonance situation. The resonance condition for a CT transition is given by the equation [22]

$$\Delta E_{\text{CT}} = h\nu_{\text{exc}}$$ (1)

Here $\Delta E_{\text{CT}}$ is the energy gap between the Fermi level of the metal and the LUMO (or HOMO) orbital from the adsorbed molecule, and $h\nu_{\text{exc}}$ is the energy of the incident photon. The shift in the pz for different anions also changes the potential where the resonance condition is satisfied; therefore, a more negative value for $E_{\text{max}}$ is expected in bromide than in chloride.

The half-width of the potential profiles is frequently used to determine the contribution of the CT mechanism in

![Fig. 4. Potential profile of adsorbed pz SER bands. 1.0 M KBr + 0.1 M pz solution. Activation procedure in the presence of pz. (a) 630 cm$^{-1}$; (b) 1235 cm$^{-1}$; (c) 1020 cm$^{-1}$; (d) 1590 cm$^{-1}$.](image-url)
allowed. This would promote the appearance of electronic bands rather than defined states. This would explain the broadening of the potential profiles with the increase in the pz concentration by the CT model.

The EM enhancement depends only on the local electromagnetic field, and, therefore, all vibrational modes of the same symmetry species should be uniformly enhanced (consistent, of course, with the SER selection rules) with respect to the applied potential. This prediction is also confirmed in Fig. 4, which shows that the SER bands of pz maximize at the same potential. A different enhancement for different modes at different potentials may be evidence for the CT mechanism, following the CT relaxation through different normal coordinates. This would lead to different \( E_{\text{max}} \) values for different vibrational bands. However, this was not observed in this work.

The independence of the \( E_{\text{max}} \) with the energy of the excitation light, presented in Fig. 5, is expected from the SER EM. However, this issue may also be addressed invoking the CT theory. In this case, the \( E_{\text{max}} \) should depend on the energy of the incident light; however, the slopes from the \( h \nu_{\text{exc}} \) vs. \( E_{\text{max}} \) lines presented by Thietke et al. [8] for the SER spectrum of py seems to be dependent on the nature of the anion. The slopes (\( (d(h \nu)/dE_{\text{max}}) \)) observed by Thietke et al. [8] increase in the order: \( \text{SO}_4^{2-} < \text{Cl}^- < \text{Br}^- \). Furtak and Macomber [25] also found an increase in the slope (\( (d(h \nu)/dE_{\text{max}}) \)) for py with increase of the \( \text{Cl}^- \) concentration. These results suggest that the dependence of \( E_{\text{max}} \) on excitation energy is very dependent on the amount of specifically adsorbed anion on the metallic surface. The explanation for that, given by Furtak and Macomber [25], is that anion adsorption induces a positive charge on the electrode, which leads to an increase in the \( \Delta E_{\text{CT}} \). Hence, a small dependence of the \( E_{\text{max}} \) on the excitation energy is expected for the SER spectrum in 1.0 M halide solutions as presented in Fig. 5. Therefore, the SER results observed in this work are consistent with both enhancement mechanisms. Despite the indication that the EM arguments seem to be more reasonable and

Table 2
Comparison of the salient features of the two most accepted surface enhancement theories

<table>
<thead>
<tr>
<th>CT mechanism</th>
<th>EM mechanism</th>
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<tbody>
<tr>
<td>1. Origin</td>
<td>Resonance process involving the incident light and the</td>
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<td></td>
<td>CT band of the metal–molecule complex (resonance</td>
</tr>
<tr>
<td></td>
<td>Raman-like process)</td>
</tr>
<tr>
<td>2. Roughness</td>
<td>Atomic scale roughness (active sites)</td>
</tr>
<tr>
<td>3. Distance dependence</td>
<td>Short range. Important only for species adsorbed</td>
</tr>
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<td></td>
<td>directly on the surface</td>
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<tr>
<td>4. Potential dependence</td>
<td>The CT band can be tuned by the applied potential;</td>
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<tr>
<td></td>
<td>therefore, the enhancement factor is potential dependent</td>
</tr>
<tr>
<td>5. Excitation wavelength dependence</td>
<td>The resonance condition depends on the excitation</td>
</tr>
<tr>
<td></td>
<td>wavelength. The potential where the SER intensity</td>
</tr>
<tr>
<td></td>
<td>maximizes (( E_{\text{max}} )) is different for</td>
</tr>
<tr>
<td></td>
<td>different incident photon energies</td>
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<tr>
<td></td>
<td>Enhancement of the local electric field due to the</td>
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<td></td>
<td>coupling of the incident photon with the metal's</td>
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<td></td>
<td>surface plasmons</td>
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<td></td>
<td>Large scale roughness (ca. 10–600 nm)</td>
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<td></td>
<td>Long range. Important even for species several</td>
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<tr>
<td></td>
<td>nanometres away from the surface, but decays with</td>
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<tr>
<td></td>
<td>the distance</td>
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<td></td>
<td>The enhancement factor does not depend on the</td>
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<td></td>
<td>applied potential; intensity changes in the potential</td>
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<td></td>
<td>profile are due to the variation of the surface</td>
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<td></td>
<td>coverage with potential</td>
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<tr>
<td></td>
<td>The enhancement factor depends on the metal dielectric</td>
</tr>
<tr>
<td></td>
<td>constant, which is wavelength dependent. The ( E_{\text{max}} ) does not shift for different incident photon energies</td>
</tr>
</tbody>
</table>
Fig. 6. Surface selection rules for IR from the image-charge theory. In this model, the electrons inside high conductivity metals will suffer a rearrangement in order to screen the external charges. (a) The molecule’s dipole is perpendicular to the surface. This leads to a resultant dipole perpendicular to the surface (in the Z direction). (b) The molecule’s dipole is parallel to the surface. The dipole image in the metal cancels the molecule’s dipole, and the resultant is null. Hence, only vibrational modes with a molecular dipole (or dipole changes) component perpendicular to the surface will have some activity.

straightforward, it is not possible to determine how much it contributes to the overall intensity based on these experimental data.

3.2. SERS selection rules

The presence of the surface can modify both the activity and the intensity of a given vibrational mode. The vibrational spectral features can be very useful for determining molecular orientation on a surface. The most straightforward surface selection rule is only vibrational modes with dipole components perpendicular to the surface will be active. This selection rule, completely true for IR and electron energy loss spectroscopies, is illustrated in Fig. 6. However, the metals’ electrical conductivities are not as high in the visible spectral region as in the IR, and consequently the molecules’ parallel components do not vanish completely in the visible region. Therefore, this selection rule does not apply exactly to surface Raman spectroscopy. Moreover, in Raman spectroscopy one must consider the polarizability tensor \( \alpha \) rather than the dipole moment and, in the specific case of SERS, one is working with a very roughened surface rather than a smooth, mirror-like one. These characteristics of enhanced Raman spectroscopy make the surface selection rules more complicated than for IR. A very comprehensive description of the SERS selection rules can be found in a review by Creighton and the references cited therein [5]. The objective of this section is to outline the salient parts of the SERS selection rules which are important to the understanding of the following part of this work.

For a situation where only the EM mechanism is important, a SERS selection rule can be exactly derived [5]. Using the Cartesian coordinates given in Fig. 7, an expression for the effective polarizability (Eq. (3)) was derived by Creighton [5]:

\[
\alpha_{eff} = \frac{9}{(\varepsilon_1 + 2)(\varepsilon_s + 2)} \begin{pmatrix} \alpha_{XX} & \alpha_{XY} & \varepsilon_s \alpha_{XZ} \\ \alpha_{YX} & \alpha_{YY} & \varepsilon_s \alpha_{YZ} \\ \varepsilon_s \alpha_{ZX} & \varepsilon_s \alpha_{ZY} & \varepsilon_s \varepsilon_s^{-1} \alpha_{ZZ} \end{pmatrix}
\]

(3)

Fig. 7. (a) The Cartesian coordinates with reference to the electrode surface \((X,Y,Z)\). (b) The molecule adsorbed to a small metal sphere model for the derivation of the SERS selection rules.
Here $X$, $Y$ and $Z$ correspond to the coordinates referenced to the electrode surface, $\alpha$ is the Raman polarizability change, $\varepsilon$ is the dielectric constant, and the subscripts $i$ and $s$ stand for incident and scattered light respectively. It is clear from the expression above that the enhancement factor can be different for each vibrational mode, depending on the values of the coefficients $\varepsilon_i$ and $\varepsilon_s$. Usually the incident and the scattered light have close frequencies, and hence, as a good approximation, one can consider $\varepsilon_i \approx \varepsilon_s \approx \varepsilon$. Assuming that the direction of the vibration determines the contribution from the polarizability tensor one can find a set of SERS propensity selection rules with some similarity to the IR. For instance, it may be seen from the Eq. (3) that modes transforming as $\alpha_{YX}$, $\alpha_{YZ}$ and $\alpha_{ZZ}$ are enhanced by the relation $|\varepsilon|^2 |\varepsilon|^4$ for excitation wavelengths were $|\varepsilon|^2 > 1$. In other words, the vibrational modes perpendicular to the metal surface should dominate the SERS spectrum. The generalization for any rough surface is straightforward and is demonstrated elsewhere [5].

The appearance of normally Raman forbidden bands in the SERS spectrum can also be explained by purely EM arguments [26]. When an inhomogeneous electromagnetic field bathes the molecule adsorbed on the metallic surface, the induced dipole moment $\mu$ is given by the expression [27]

$$\mu = \alpha E + \frac{1}{3} A \nabla E$$  \hspace{1cm} (4)

Here $A$ is a third rank tensor, called the quadrupole polarizability, operating over the field gradient. This tensor transforms as the hyperpolarizability, but it has a completely different physical meaning. $\alpha$ is the polarizability, $E$ is the electric field and $\nabla E$ is the field gradient. The vector's and tensor's Cartesian components are omitted for simplification. The second term in the induced dipole expression is very important for rough surfaces, and its contribution decreases with the distance from the electrode surface. The tensor $A$ transforms as a product of three translations. Considering an image-charge approach, the translations in the $X$ and $Y$ directions should yield a $-X$ and $-Y$ image inside the metal (see Fig. 6(b)). The $Z$ direction translation vector, however, would have an image with the same sign and intensity, yielding a positive resultant (Fig. 6(a)). As the quadrupole polarizability can be thought of as a product of three translations, the products that do not change sign on the image-charge transformation would be active. Thus, the $A_{ZZZ}$, $A_{ZXY}$, $A_{YZZ}$ and $A_{XXZ}$ should be surface active, and the $A_{XXX}$, $A_{YXY}$, $A_{ZXX}$ and $A_{XZZ}$ produce surface inactive vibrations [26]. It is also important to point out that the assumption that $X$ and $Y$ components are completely screened by the surface is not fully valid when one is working in the visible range of the electromagnetic spectrum [26].

Owing to the expectation of a preferential enhancement of components in the $Z$ direction, the EM selection rules are widely applied in SERS studies for the determination of the molecular orientation on the surface.

The CT enhancement mechanism contribution occurs via a resonance Raman (RR) process, involving a charge transfer between the Fermi level of the metal and either the HOMO or LUMO orbitals of the adsorbed organic molecule [5]. The RR theory [28] predicts that the symmetric modes, enhanced by an $A$-term mechanism, should dominate the spectrum. The $B$-term contribution is non-zero if the irreducible representation of the normal coordinate is contained in the direct product of the irreducible representation between the resonance and the mixed excited states [28]. It is clear that the $B$-term can account for the eventual normal Raman-forbidden bands that arise in the RR or in the SERS spectrum.

The presence of normally Raman-forbidden bands in the SERS spectrum can also be explained in the CT mechanism as a consequence of the molecular symmetry perturbation due to the surface. For instance, a free $pz$ molecule with $D_{2h}$ symmetry could lose its centre of symmetry due to adsorption and become a $C_{2v}$ complex. The two most probable orientations for $pz$ adsorbed on a metallic surface are presented in Fig. 8. An edge-on orientation is also possible, but not probable from the chemical point of view. All modes are Raman-allowed under $C_{2v}$ symmetry. The correlation table between $D_{2h}$ and $C_{2v}$ symmetries is given in Fig. 9.

3.3. The molecular orientation of $pz$ on silver electrodes

In order to facilitate the following discussion, the SERS-active Raman bands of $pz$, sorted according to intensity and symmetry species, are collected in Table 3.
Considering the metallic and the molecular axis, defined in Fig. 7 and Fig. 8 respectively, it is clear that for an end-on adsorption the molecular zx plane coincides with the surface XZ. The EM predicts that the vibrational modes containing the \( \alpha_{zz} \) will be the most intense, followed by the \( \alpha_{xy} \) or \( \alpha_{xz} \), and then the modes containing the \( \alpha_{yy} \). In the \( D_{2h} \) point group, \( \alpha_{zz} \), \( \alpha_{xy} \), \( \alpha_{xz} \), and \( \alpha_{yy} \) are contained in the \( A_g \), \( B_{2g} \), \( B_{3g} \) and \( B_{1g} \) representations respectively. In fact, the \( A_g \) modes dominate the SER spectrum of pz adsorbed on silver. The 1590 cm\(^{-1}\) (8a) ring mode, is the most intense band for the potential of maximum intensity. The 8a mode’s polarizability change is mainly in the molecular z direction (see Fig. 1, region 3). The \( B_{2g} \) modes show up with medium intensity except for the ca. 1324 cm\(^{-1}\) band (\( B_{3g} \), number 3) which is weak. Only one \( B_{3g} \) mode is observed as a weak feature at 741 cm\(^{-1}\). However, the other \( B_{3g} \) mode is expected at ca. 973 cm\(^{-1}\) [4], and it may be concealed by the strong ring-breathing mode. The single \( B_{1g} \) mode is observed at ca. 916 cm\(^{-1}\) as a very weak band. Therefore, this analysis, involving all Raman-allowed bands of pz, is consistent with an end-on adsorption.

Considering that a CT complex is formed and its electronic energy is in resonance with the excitation radiation, one can also expect the totally symmetric modes to be enhanced by an A-term mechanism.

Thietke et al. [8] endorse the photon-driven charge transfer (PDCT) model, and suggest that the SER spectrum should have some analogy to the inelastic scattering of the electron via a negative ion resonance known as shape resonance. According to the selection rules in shape resonance, only totally symmetric modes are excited when the \( \pi^+ \) orbitals corresponding to the affinity levels are non-degenerate, as in the pz molecule. The shape resonance of pz presents a vibronic progression entirely dominated by the 1020 cm\(^{-1}\) ring-breathing (1) mode [29]. This vibrational mode is strong in the SER spectrum and its polarizability also changes along the N–N axis (Fig. 1, region 3).

The low frequency region of the pz’s SER spectrum is, in contrast to aqueous pz, dominated by the 630 cm\(^{-1}\) band (6a) rather than the ca. 700 cm\(^{-1}\) band (6b). The former mode changes its polarizability along the molecule’s N–N axis, but less so for the latter (see Fig. 1 for the vibrational mode descriptions). The 6a and the 9a modes dominate the RR spectrum involving the first electronically excited state of pz (\( B_{2u} \leftrightarrow A_g \)) [30], and the ring-breathing mode together with the 6a mode dominate the RR spectrum involving the second excited state of pz (\( B_{3u} \leftrightarrow A_g \)) [31]. Therefore, an additional contribution to these modes from a CT cannot be discarded.

Moreover, the RR spectrum of pz contains the 10a out-of-plane mode of \( B_{1g} \) symmetry at ca. 916 cm\(^{-1}\) with fair intensity. This band is activated in the RR spectrum due to the vibronic coupling between the electronic excited states (\( B_{2g} \otimes B_{3u} \)). However, this band is very weak in the SERS (Table 3).

The chemical enhancement mechanism explains the presence of forbidden bands as a result of symmetry lowering due to adsorption (Fig. 8). For the \( C_{2v} \) surface complex the new Raman-allowed bands (\( 2A_g + 4B_{1u} + 2B_{2u} + 4B_{3u} \)) are given in the correlation table (Fig. 9). However, Moskovits et al. [9] argue that the frequency shifts for the pz bands from the electrode surface compared with the peak positions from pz in aqueous solutions are not sufficient to justify complex formation.

The 360 cm\(^{-1}\) band is an \( A_u \) out-of-plane band. It is practically impossible to detect this band in the IR of pz [16] because the \( A_u \) mode does not contain any component from the dipole moment. However, this mode contains the \( \alpha_{yz} \) component of the quadrupole polarizability, and hence it is expected to be surface active by the field gradient model [26], and it is observed (Fig. 1).

Moreover, following the field gradient mechanism [26], the bands that contain the \( \alpha_{zz} \) components should also be enhanced. For pz under \( D_{2h} \) symmetry, \( \alpha_{zz} \) is contained in the \( B_{1u} \) modes. In fact, the \( B_{1u} \) mode bands are observed with a very weak intensity at 1118 and 1040 cm\(^{-1}\).

Some \( B_{2u} \) out-of-plane bands also show up with weak intensity, but are undoubtedly present at 430 and 797 cm\(^{-1}\).

### Table 3

<table>
<thead>
<tr>
<th>Species</th>
<th>Frequency/cm(^{-1})</th>
<th>Number</th>
<th>Components</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_g )</td>
<td>3030 (s)</td>
<td>2</td>
<td>( \alpha_{xx}, \alpha_{yy}, \alpha_{zz} )</td>
</tr>
<tr>
<td>1390 (vs)</td>
<td>8a</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1215 (m)</td>
<td>11 + 16b</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1235 (s)</td>
<td>9a</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1020 (vs)</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>630 (m)</td>
<td>6a</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( B_{1g} )</td>
<td>916 (w)</td>
<td>10a</td>
<td>( \alpha_{xy} )</td>
</tr>
<tr>
<td>3020 (m)</td>
<td>7b</td>
<td>( \alpha_{xz} )</td>
<td></td>
</tr>
<tr>
<td>1514 (m)</td>
<td>8b</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1324 (w)</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>700 (m)</td>
<td>6b</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( B_{2g} )</td>
<td>741 (w)</td>
<td>4</td>
<td>( \alpha_{yz} )</td>
</tr>
<tr>
<td>( A_u )</td>
<td>360 (w)</td>
<td>16a</td>
<td>( A_{yz} )</td>
</tr>
<tr>
<td>( B_{1u} )</td>
<td>1118 (vw)</td>
<td>18a</td>
<td>( A_{zzz}; A_{yyz}; A_{zzx} )</td>
</tr>
<tr>
<td>1040 (vw)</td>
<td>12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( B_{2u} )</td>
<td>797 (w)</td>
<td>11</td>
<td>( A_{yyz}, A_{zxz}, A_{yyz} )</td>
</tr>
<tr>
<td>430 (w)</td>
<td>16b</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The \( B_{2u} \) modes contain the \( A_{yy} \), \( A_{zz} \) and \( A_{zz} \) terms of the quadrupole polarizability; hence, these bands are expected to be surface inactive for a pz molecule adsorbed perpendicular to the surface by the field gradient model. There are several possibilities that would explain the presence of these out-of-plane modes. First of all, one can argue that these modes are evidence that pz lies flat on the electrode surface. However, the large enhancement for the in-plane CC band at 1590 cm\(^{-1}\), together with the large intensity of all modes with polarizability change in the N–N axis direction, argues against this hypothesis. A second explanation is illustrated in Fig. 10. As the potential becomes negative, some halide anion, which stabilizes pz in the end-on position, leaves the electrode surface. In this case, the pz molecules could laterally interact with each other, and they could tilt a little towards the electrode surface. This tilted configuration could account for both the in-plane and out-of-plane modes. A third, and most probable possibility is that the presence of unexpected ‘surface inactive’ bands for the end on adsorption just reflects the limitation of the field gradient model. In order

![Image of molecular structures and Raman spectra](image)

Fig. 10. (a) For a positively charged electrode pz is coadsorbed with bromide ions. This situation can stabilize the pz molecule in an end-on configuration. (b) As the electrode charge becomes negative, the bromide ions leave the metallic surface. This situation permits a better lateral interaction between pz molecules, and the molecules can tilt on the metallic surface.

![Image of Raman spectra](image)

Fig. 11. Spectra of pz adsorbed on a silver electrode at more negative potentials. 1.0 M KBr + 0.1 M pz solution. Activation procedure in the presence of pz. The arrow indicates the raising of new bands due to the electrochemical reduction of pz. (a) – 800 mV; (b) – 900 mV; (c) – 1000 mV; (d) – 1100 mV; (e) – 1200 mV.

![Image of chemical reactions](image)

Fig. 12. Pz reduction at pH values higher than 2.5 leads directly to the formation of the 1,4-dihydropyrazinium cation [32,33] (compound A). The cation can be reversibly re-oxidized to pz. However, dihydropyrazine can also undergo a different chemical process, which can lead to ring opening, ring substitution and polymerization. Some of these chemical products can be either re-oxidized or trapped in the electrode surface, and they are called in the text “compound B”.
Table 4
Vibrational frequencies from electrochemically decomposed pz in 1.0 M Br\textsuperscript{−} medium. Compound A was obtained at potentials more negative than −900 mV. Spectrum from compound B was obtained in the range between ca. −450 to −750 mV, only after the electrochemical reduction of pz has occurred.

<table>
<thead>
<tr>
<th>Compound A, ( \nu / \text{cm}^{-1} )</th>
<th>Compound B, ( \nu / \text{cm}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>295</td>
<td>875</td>
</tr>
<tr>
<td>520</td>
<td>963</td>
</tr>
<tr>
<td>620</td>
<td>1062</td>
</tr>
<tr>
<td>725</td>
<td>1181</td>
</tr>
<tr>
<td>751</td>
<td>1496</td>
</tr>
<tr>
<td>763</td>
<td>1617</td>
</tr>
<tr>
<td>906</td>
<td></td>
</tr>
<tr>
<td>950</td>
<td></td>
</tr>
<tr>
<td>1070</td>
<td></td>
</tr>
<tr>
<td>1166</td>
<td></td>
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<td>1320</td>
<td></td>
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</tr>
<tr>
<td>1640</td>
<td></td>
</tr>
<tr>
<td>3060</td>
<td></td>
</tr>
</tbody>
</table>

The reduction of pz in an acidic medium is a well-known process and leads to the formation of the 1,4-dihydropyrazinium cation [32,33]. Some 1,4-dihydropyrazinium SERS bands on silver colloid were reported by Muniz-Miranda et al. [11]. They also confirmed the presence of 1,4-dihydropyrazinium in monomeric and dimeric forms by mass spectroscopy. These compounds were formed from an excess of reducing agent during the formation of the silver colloid [10,11]. Electrochemical work suggests the possibility of a ring-opening process in an acidic medium [33]. The 1640 cm\textsuperscript{−1} reduced pz band (compound A) can be assigned to a C=C ring stretch. All other bands presented in Table 4 for compound A can also support the formation of the 1,4-dihydropyrazinium cation. However, one can also suggest alternative assignments for bands in Fig. 12; thus, other compounds cannot be ruled out. For instance, the 520 cm\textsuperscript{−1} band may be due to a C–Br stretch mode [34].

An important point to be extracted from Table 4 is the observation that the bands of compound B do not show up, either in the activation procedure in the absence of pz or before an electrode potential more negative than −900 mV. Comparing the vibrational frequencies in Table 4 to some band frequencies reported in the literature of SERS of pz (and tabulated in Table 1) we conclude that some authors have incorrectly assigned bands due to trapped compound A or B to pz. This raises again the question about what is the best activation procedure for SERS [35]. The activation procedure in the presence of the organic molecule yields a better signal, but the spectrum obtained in that way must always be compared with the spectrum after an activation procedure in the absence of the organic molecule. Any eventual differences in the spectra obtained from these two activation procedures may be interpreted as arising from an electrochemical reaction and subsequent trapping of decomposition products.

3.4. The electrochemical reduction of pz

Spectra of pz in a bromide medium (Fig. 11) reveal that the organic molecule is reduced at potentials more negative than −900 mV; a new species is formed which will be called compound A. Analysing Fig. 11, one can observe that new bands appear and the pz bands disappear simultaneously. When the potential is switched back toward the positive direction, anodic current is observed. The majority of this re-oxidation current is due to pz formation. However, some other species (compound B) is also formed, as shown in Fig. 12. At this point, the SERS signal is weak and a new ORC is needed to regenerate the spectra. In the new SER spectrum, after the formation of reduced pz and subsequent re-oxidation, some bands due to compound B persist. The frequencies of the bands due to these pz decomposition products are presented in Table 4. Thietke et al. [8] reported the presence of reduced pz at the electrode surface by SERS; however, they claimed that the electrochemical process is reversible in a sulphate medium and the bands of these reduced products were not observed at more positive potentials.

3.5. General discussion and comparison with the literature

The main features of the spectra presented in this work agree well with the literature. All work, except that of Dornhaus et al. [7] who worked in oxygen-containing solution and recorded a transient spectrum (acquisition time of 25 ms), reported that the symmetrical modes yield the most enhanced bands. However, some authors have reported several forbidden bands that we have not observed [6–8]. It is expected that more forbidden bands will be observed from pz adsorbed on cold deposited silver [9] than for pz on the electrode surface; the geometry of the silver bumps from the cold deposited method favours the field gradient mechanism. This mechanism may be damped at the electrode surface due to the halides’ coadsorption. However, from Tables 1 and 3, it is possible to discern that certain ‘forbidden bands’ observed in some of the previous electrochemical SERS studies can be due to pz decomposition products, as suggested before by Sbrana and co-workers [11]. Since all previous work has activated the
electrode in the presence of pz, some trapped pz species, like compounds A and B reported here, could remain on the electrode surface.

Another point is the importance of the $B_{1g}$ (12) ring mode at 1030 cm$^{-1}$ for the determination of the orientation of pz at the electrode surface. Several authors have agreed that the presence of this band determines the molecular orientation on the electrode. Hallmark and Campion [36] studied the NRS of pz adsorbed on a silver single-crystal. They used a weak presence of this mode to draw the conclusion that pz changes its orientation from flat on Ag(111) to tilted on Ag(110). Based on Hallmark and Campion’s results, Bhattacharjee [37] confirmed his theory for surface selection rules. Huang and Wu [12] and Zhong and Wu [13] stated that the absence of this band from a gold electrode can lead to the false conclusion that the molecule lies flat on the electrode surface. The ca. 1030 cm$^{-1}$ band is very strong in the aqueous pzH$^+$ complex (Fig. 1, region 3), but it always shows up as a very weak feature at the electrode, even in the Huang and Wu spectra. However, this band showed up with an appreciable intensity in the cold deposited silver experiment [9]. The NRS of pz adsorbed on a silver surface [36] had low signal-to-noise, and the presence of this band is uncertain. Observing this mode’s description in Ref. [15], one can qualitatively notice a significant contribution from polarizability components parallel to the electrode surface, when an end-on adsorption is inferred. Moreover, this mode is forbidden in the NRS of pz, and its presence on the electrode is possible due to the field gradient enhancement. This enhancement mechanism does not yield a reliable set of selection rules necessary to infer the molecular orientation, as we demonstrate in this work. From the above arguments, we do not agree that the presence or absence of this mode is enough to draw conclusions about the orientation of pz adsorbed on a metallic surface. The orientation of pz on the electrode surface must be inferred from the intensity of significant perpendicular modes, compared with the intensities of significant parallel modes.

In order to illustrate the discussion above, we examine the spectra of pz on a colloid, presented by Muniz-Miranda et al. [10-11]. These spectra show several similarities to the aqueous pz spectrum, including the fact that the 1020 cm$^{-1}$ band is the strongest one, being about eight times stronger than the 1595 cm$^{-1}$ band. They conclude that the 1595 cm$^{-1}$ band is enhanced two-fold, and the out-of-plane CH bending (10a) at 920 cm$^{-1}$ is enhanced four-fold. The most enhanced symmetric mode is the 1225 cm$^{-1}$ band. The 636 cm$^{-1}$ band is only enhanced two-fold, and it is still weaker than the 700 cm$^{-1}$ band. Muniz-Miranda et al. suggest an end-on adsorption based on the presence of a band at ca. 220 cm$^{-1}$, assigned to the Ag–N mode. The presence of this band was suggested from an asymmetry of the Ag–Cl band. Despite the supposed presence of this Ag–N band, which points to an end-on adsorption, all other evidence seems to support either tilted or flat pz adsorption on the colloid. It is also important to point out that the asymmetry of bands in the metal–halide region, also observed in this work (Fig. 2), may just reflect the existence of more than one type of SERS active site for halide [17,18]. Moreover, the colloid spectrum is also similar to that presented by Moskovits et al. [9] in the low pz coverage experiment, except for the absence of the 1030 cm$^{-1}$ mode. Hence, we conclude that the molecular orientation of species adsorbed on a metallic surface must be inferred from the analysis of a set of in-plane and out-of-plane vibrational modes. The presence or absence of weak bands is not sufficient; the entire spectrum should be considered.

4. Conclusion

Two activation procedures were used for the SERS study of pz adsorbed on a silver electrode: these involved an ORC either in the presence or in the absence of pz. The band positions were not sensitive to the activation procedure, but the activation in the presence of pz yielded better signal-to-noise. The pz spectra obtained from an electrode activated in the presence of pz may include additional bands from trapped species from the electrochemical reduction of pz; therefore, care must be taken in the activation procedure to avoid pz reduction.

The SERS intensity and the potential profiles proved to be independent (within experimental error) of both the pz concentration and the excitation wavelength.

The pz molecule stands up and is bonded to the electrode by a lone electron pair; however, a tilted configuration cannot be totally excluded. This conclusion was drawn from the observation of a greater enhancement from modes with polarizability components perpendicular to the electrode surface, when compared with the modes parallel to the surface. The main features presented here agree well with the literature; however, some previous misunderstandings have been clarified.

Acknowledgements

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