SERS studies of monoprotonated pyrazine (pyrazinium) cations adsorbed onto positively charged silver electrodes

A.G. Brolo and D.E. Irish

Abstract: The surface-enhanced Raman scattering (SERS) spectra of monoprotonated pyrazine cations adsorbed on silver electrodes have been measured. The molecular orientation of the pyrazinium cation is dependent on the electrode potential. At potentials more positive than $-170 \text{ mV}$ the monoprotonated pyrazine is adsorbed end-on. However, the spectral features suggest a flat orientation as the potential becomes more negative than $-300 \text{ mV}$. Monoprotonated pyrazine cations with both orientations can coexist at potentials between these limits. The adsorption of the positive ion to a positively charged electrode is mediated by specifically adsorbed bromide ions.

Key words: SERS; monoprotonated pyrazine cation, silver electrode, pyrazinium.

Résumé: On a mesuré les spectres de diffusion Raman rehaussés par la surface «SERS» de cations de pyrazine monoprotonnée adsorbée sur des électrodes d’argent. L’orientation moléculaire du cation pyrazinium dépend du potentiel de l’électrode. À des potentiels plus positifs que $-170 \text{ mV}$, la pyrazine monoprotonée est adsorbée par son extrémité. Toutefois, les caractéristiques spectrales suggèrent que l’orientation est plate lorsquels le potentiel devient plus négatif que $-300 \text{ mV}$. Des cations de pyrazine monoprotonnée ayant les deux orientations peuvent coexister à des potentiels entre ces limites. L’adsorption de l’ion positif sur une électrode chargée positivement se fait avec l’aide d’ions bromure adsorbés d’une façon spécifique.

Mots clés: diffusion Raman rehaussée par la surface «SERS», cation pyrazine monoprotoné, électrode d’argent, pyrazinium.

[Intégré par la rédaction]

Introduction

Pyrazine is a centrosymmetric molecule that belongs to the $D_{2h}$ point group. Protonation of one nitrogen will suppress the centre of inversion and reduce the symmetry to $C_{2v}$. This symmetry lowering will “activate” all the pyrazine vibrational modes in the Raman spectrum. However, pyrazine is a very weak base, and its low $pK_a$ values ($pK_{a1} = 0.65$ and $pK_{a2} = -5.8$) (1) make protonation possible only in very acidic media.

A Raman spectral study of pyrazine and its protonated forms in aqueous solution has been performed in our laboratory (2). By observation of the shifts of the bands from the positions measured for neutral solutions, it has been possible to identify the unique characteristic bands of unprotonated pyrazine and its two protonated forms. The majority of the vibrational bands of the monoprotonated pyrazine ($pzH^+$) were identified and assigned (2). The diprotonated pyrazine cation spectrum was only observed from very concentrated $\text{H}_2\text{SO}_4$ and $\text{HClO}_4$ solutions, and the presence of strong bands from these acids masked some of its bands (2). The positions of these masked bands have been predicted theoretically (3). The ab initio calculations for pyrazine and its two protonated forms provided useful confirmation of the assignments of the observed bands within 10% accuracy.

The identification and assignment of the vibrational bands from pyrazine and monoprotonated pyrazinium cation ($pzH^+$) in solution proved to be useful in the interpretation of the Raman spectrum of pyrazine adsorbed onto metallic surfaces (4). The positions of the vibrational bands in the surface-enhanced Raman scattering (SERS) spectrum of pyrazine adsorbed on a polycrystalline silver electrode are more similar to those of aqueous pyrazine than those of its monoprotonated derivative. However, several “forbidden” pyrazine modes were activated by the electrode surface (4). The presence of Raman forbidden bands in the SERS spectrum of pyrazine can be explained either by the “chemical” (charge transfer (CT)) or by the “electromagnetic” enhancement mechanisms (5).

The intensities of all bands in the SERS spectrum of pyrazine are potential dependent, and their maxima depend on the electrolyte and on the activation medium (4). The spectrum is mainly dominated by the ring stretch (number $B_1$) mode at ca. $1590 \text{ cm}^{-1}$. The ring breathing (number 1) mode at ca. $1019 \text{ cm}^{-1}$ is the second most intense band, followed by the other $A_e$ modes at $630$ and $1235 \text{ cm}^{-1}$. Vibrational bands at ca. $360$, $432$, $700$, $1225$, and $1520 \text{ cm}^{-1}$ were also observed.

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New features have been observed in the SERS spectrum of pyrazine adsorbed on a silver electrode immersed in a 1.0 M KBr solution when the applied potential is more negative than \(-900\) mV (6). These new bands were assigned to the main reduction product of pyrazine, the 1,4-dihydropyrazinium cation (7, 8). The 1,4-dihydropyrazinium cation, formed at negative potentials, can be adsorbed on the electrode surface even at potentials more positive than the pzc for silver in that medium. In this case, the reduced pyrazine cation binds to the halide layer (6). The halide, which is adsorbed on the positively charged metal surface, acts like a bridge. The same phenomenon has been observed for the adsorption of other cations like pyridinium (9) and tetramethylammonium (10). Hence, the presence of the 1,4-dihydropyrazinium cation on the silver electrode at positive potentials suggests that the monoprotonated pyrazine can also be adsorbed on a positively charged silver electrode by a similar mechanism. We have thus explored the adsorption of \(p\)Hz on a polycrystalline silver electrode in acidic media. This work complements the preliminary results that we presented elsewhere (11).

**Experimental section**

**Reagents**

The following chemicals were used without further purification: pyrazine 99+%, from Aldrich; KBr AnalR grade, from BDH; and concentrated HClO\(_4\), from Baker. All solutions were prepared with Milli-Q-water.

**Electrochemistry**

The three-electrode spectrotrochemical cell has been described elsewhere (12). A potentiostat PAR model 273 was used to control the potential applied to 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 \(\mu\)m. The electrode was rinsed with an abundant amount of Milli-Q-water, sonicated, rinsed again, and transferred to the spectrotrochemical cell. The solution was degassed with Ar for 0.5 h prior to the experiment, and a gentle stream of Ar was kept on during the data acquisition.

**Activation procedure**

The process of roughening the metal surface electrochemically, in order to create the necessary SERS active sites, is called the activation procedure. In this work we activated the electrode electrochemically by a sequence of Oxidation–Reduction Cycles (ORCs). ORCs were performed on the silver electrode from an aqueous solution containing 1.0 M KBr and 1.0 M HClO\(_4\) by sweeping from \(-800\) to \(-50\) mV at 5 mV/s. The potentiostat was turned off, and pyrazine was added to the system. This sequence prevents decomposition, which might occur during the ORC; trapped decomposition products have been observed when the analyte was present during the ORC (6). The pyrazine concentration used in all experiments was 0.1 M. After pyrazine was introduced into the system, the potentiostat was switched on again, the ORC cycle was resumed, and the SERS spectrum of pyrazinium adsorbed on silver was recorded at the desired potential values.

**Raman spectra**

Raman spectra were measured with a Dilor OMARS 89 spectrometer equipped with an optical multichannel analyzer (OMA). The intensified diode array (512 diodes) detector was thermoelectrically cooled to ca. \(-10^\circ\)C. The spectrometer was interfaced to an IBM computer. The data were transferred to an IBM 486 computer on which baseline correction, band-fitting, and plotting programs were available. The spectra were excited by using a 514.5 nm (100 mW at the head) line from a Coherent Innova 70 argon ion laser operated at a 1 s cycle. The chopping is a feature of the Dilor OMARS 89 spectrometer to improve signal-to-noise; it has the added advantage of diminishing photodegradation.

**Results and discussion**

Figure 1 shows the spectrum obtained for pyrazine adsorbed from a 1.0 M KBr + 1.0 M HClO\(_4\) + 0.1 M pyrazine solution onto the SERS activated silver surface at the open circuit potential (OCP) for several spectral regions. The band positions and assignments are presented in Table 1. Table 1 also shows the band positions of the pyrazine SERS spectrum obtained from a neutral solution (4) and the pyrazine and monoprotonated pyrazine bands from aqueous solution (2). A comparison between the spectrum presented in Fig. 1 and the SERS spectrum of pyrazine adsorbed from a nonacidic solution shows striking differences in the peak positions and intensities. It has been proposed that the adsorption of neutral pyrazine onto a metallic surface would remove the molecular center of symmetry (13). Consequently, the molecular symmetry should be reduced from \(D_{2h}\) to \(C_{2v}\) due to the adsorption. In this case, it can be expected that the spectrum of adsorbed neutral pyrazine (under \(C_{2v}\) symmetry) should have some similarities with the spectrum of the monoprotonated pyrazine cation (also \(C_{2v}\)) in solution. However, as observed in Table 1, the vibrational wave numbers found for pyrazine adsorbed onto a silver electrode from acidic solution more closely match the wave numbers of the monoprotonated pyrazine cation in solution, and the peak positions in the SERS spectrum of pyrazine adsorbed from neutral solution are more similar to those from the pyrazine spectrum of the aqueous solution. This is an indication that symmetry reduction, due to formation of a metal–organic molecule complex, is not a necessary consequence of adsorption, and that the interaction of pyrazine with the metal is not strong enough to induce a symmetry change.

The SERS spectra at potentials more positive than ca. \(-100\) mV were time dependent. The SERS signal decreased with time, and the rate of decrease became faster as the potential became more positive. A simple explanation is that a silver bromide film is formed during the silver oxidation step, and this film quenches the SERS effect, which is a near-surface phenomenon. The time dependence of the SERS signals made the study of medium intensity and weak bands very difficult at these potentials. Hence, we focused our work in the 1000, 1200, and 1600 cm\(^{-1}\) regions where the strongest bands were found.
Fig. 1. SERS spectrum of pyrazinium on a silver electrode adsorbed from a 1.0 M KBr + 1.0 M HClO₄ + 0.1 M pyrazine solution at the open circuit potential (OCP). The asterisks (*) mark the bands that are not present in the SERS spectrum of pz adsorbed from neutral solution (see text). The plus sign (+) marks the ClO₄⁻ symmetrical stretch mode.

Table 1. Vibrational frequencies (in cm⁻¹) and assignments for pyrazine (pz) in solution; monoprotonated pyrazine (pzH⁺) in solution; pyrazine adsorbed from acidic solution onto silver electrodes; pyrazine adsorbed from nonacidic solutions onto silver electrodes.

<table>
<thead>
<tr>
<th>Adsorption from a 1.0 M KBr + 1.0 M HClO₄ + 0.1 M pz solution</th>
<th>Adsorption from a 1.0 M KBr + 0.1 M pz solution, E = 700 mV (from ref. 2)</th>
<th>Pyrazine in solution, E = 0 mV (from ref. 2)</th>
<th>Vibrational assignments. a</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCP</td>
<td>E = -100 mV b</td>
<td></td>
<td>1602 (s)</td>
</tr>
<tr>
<td>411  (w)</td>
<td>417 (vwv)</td>
<td>432 (w)</td>
<td>B₃u/B₂ (16b)</td>
</tr>
<tr>
<td>602  (m)</td>
<td>606 (w)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>611  (sh)</td>
<td>688 (m)</td>
<td>630 (m)</td>
<td>A₄u/A₁ (6a)</td>
</tr>
<tr>
<td>710  (w)</td>
<td>697 (w)</td>
<td>692 (w)</td>
<td>B₄u/B₁ (6b)</td>
</tr>
<tr>
<td>898  (m)</td>
<td>898 (vw)</td>
<td>702 (m)</td>
<td>B₄u/A₁ (10a)</td>
</tr>
<tr>
<td>934  (s)</td>
<td>934 (s)</td>
<td></td>
<td>ClO₄⁻</td>
</tr>
<tr>
<td>1002 (s)</td>
<td>1002 (s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1018 (s)</td>
<td>1018 (s)</td>
<td>1019 (vs)</td>
<td>A₄u/A₁ (1)</td>
</tr>
<tr>
<td>1031 (sh)</td>
<td>1031 (sh)</td>
<td>1020 (vs)</td>
<td>B₄u/A₁ (12)</td>
</tr>
<tr>
<td>1090 (w)</td>
<td>1112 (w)</td>
<td></td>
<td>B₄u/A₁ (18a)</td>
</tr>
<tr>
<td>1222 (s)</td>
<td>1222 (s)</td>
<td>1223 (m)</td>
<td>A₄u/A₁ (9a)</td>
</tr>
<tr>
<td>1616 (vs)</td>
<td>1616 (vs)</td>
<td>1618 (m)</td>
<td>A₄u/A₁ (11 + 16b)</td>
</tr>
<tr>
<td>1635 (sh)</td>
<td>1635 (sh)</td>
<td>1590 (vs)</td>
<td>A₄u/A₁ (8a)</td>
</tr>
</tbody>
</table>

 a The symmetry species are presented for both D₄h (for pyrazine) and C₂v (for monoprotonated pyrazine) point groups (D₂h/C₂v). A correlation table was used (see ref. 2).
 b Perpendicular-adsorbed pzH⁺.
 c Flat-adsorbed pzH⁺.
 v = very; s = strong; m = medium; w = weak; sh = shoulder.

Figures 2, A–C, show the SERS spectra of pyrazine adsorbed from acidic solution on a silver electrode at several potentials. The point of zero charge for silver in bromide medium is expected to be more negative than -900 mV (14) and, thus, the surface charge is positive. As the potential is swept to values more positive than -170 mV, the band intensity at 1002 cm⁻¹ decreases, and one can just notice two bands near 1020 cm⁻¹ at potentials close to the onset of the silver oxidation (around -100 mV). These two bands coalesce into a broad envelope that can be resolved using a band-fitting computer program. The experimental track in this region and its band-fitted components are presented in Fig. 3. From the

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Fig. 2. SERS spectrum of pyrazinium on a silver electrode adsorbed from a 1.0 M KBr + 1.0 M HClO₄ + 0.1 M pyrazine solution at several potentials. For (A): (a) −160 mV; (b) −250 mV; (c) −340 mV. For (B): (a) −170 mV; (b) −235 mV. For (C): (a) −170 mV; (b) −250 mV; (c) −310 mV.

band-fitting analysis one can locate the positions of these two bands at ca. 1018 and at ca. 1031 cm⁻¹, respectively. Just one band is observed at 1222 (Fig. 2B) and 1616 cm⁻¹ (Fig. 2C) at potentials more positive than −170 mV.

As the potential was swept to less positive values, the SERS intensity of pzH⁺ was recovered following the silver ion reduction around ca. −200 mV. In this case, the 1002 cm⁻¹ band was present and it was more intense than the envelope at ca. 1020 cm⁻¹. The 1002 cm⁻¹ band is the only one left in the spectrum in the 1000 cm⁻¹ region at potentials more negative than ca. −280 mV (Fig. 2A). Two bands showed up in the 1200 cm⁻¹ region after the silver ion reduction (Fig. 2B), one band at 1222 cm⁻¹ and another at ca. 1200 cm⁻¹. The 1616 cm⁻¹ intensity decreased as the potential became negative (Fig. 2C), and its position remained unchanged. This band vanished completely near −300 mV.

The results presented above are consistent with an adsorption of pyrazinium cation with different orientations at
different potentials. One adsorption orientation is predominant during the silver oxidation ($E > -170$ mV), and the other dominates at potentials more negative than $-300$ mV. These two different orientations of adsorbed monoprotonated pyrazine can coexist on the metallic surfaces at intermediate potentials. Actually, the pyrazinium ion spectrum at OCP presented in Fig. 1 is an example of this. The two different orientations proposed for the monoprotonated pyrazine cation are illustrated in Fig. 4.

The surface selection rules for SERS predict that the vibration modes with polarizability changes perpendicular to the electrode surface will be more enhanced than the parallel ones (5). Pyrazine adsorbed from neutral solution is thought to bind to the metallic surface by means of one of its nitrogen atoms (4). This end-on adsorption mode is confirmed by a SERS spectrum dominated mainly by the 630, 1019, 1225, and 1590 cm$^{-1}$ bands; for end-on adsorption these bands have components perpendicular to the surface.

The most predominant band in the p$zH^+$ spectrum at potentials more positive than $-170$ mV is the ring stretch mode $8a$ at 1616 cm$^{-1}$ (Fig. 2C). This band is, at least, 3 times more intense than the ring breathing mode at ca. 1000 cm$^{-1}$. The $8a$ mode is more intense than the ring breathing mode in the SERS spectra of the perpendicular-adsorbed pyrazine (4). Even considering that a CT contribution may be relevant for the large intensity of the band at 1616 cm$^{-1}$ (15), the intensity ratio between this mode and the ring breathing mode (at ca. 1000 cm$^{-1}$), observed in Fig. 2, suggests that pyrazinium is adsorbed end-on at those potentials where the silver oxidation occurs. The presence of the 1031 cm$^{-1}$ $\delta$ ring mode (number 12) also supports an end-on adsorption. This mode is forbidden in the normal Raman spectrum of pyrazine, but becomes active (with very weak intensity) in the SERS spectrum of pyrazine (4). It also appears with fair intensity in the SERS spectrum of end-on adsorbed pyridine (7). On the other hand, this mode is completely absent in the flat-adsorbed benzene SERS spectrum (16).

Another point to be addressed is how a positive monoprotonated pyrazine can adsorb on a positively charged electrode (the pzc for silver in this bromide medium is expected to be more negative than $-900$ mV (14)). It is well known in the literature that positive species can use a halide layer as bridge to adsorb onto a positively charged surface (6, 9, 10). During the silver oxidation, a AgBr film is expected to form. It is possible that film dissolution can occur in a highly concentrated halide medium, by formation of $\text{(AgBr)}_{x}\text{(Cl)}$ anions. We can conclude that the pyrazinium cation is bound to either a halide or to the $\text{(AgBr)}_{x}\text{(Cl)}$ and these anions are adsorbed to the positively charged electrode (see Fig. 4a). A low wave number band at 150 cm$^{-1}$, attributed to adsorbed Br$^-$, decreases in intensity as the electrode is made more negative; concomitantly the band of p$zH^+$ decreases in intensity. These observa-
tions are consistent with the potential-dependent Br$^-$ surface coverage determined electrochemically (14).

Different features in the pH$^+$ spectrum were observed when the potential sweep was continued in the negative direction and the reduction of the silver oxidation products occurred. The Ag$^+$ ions reduced to Ag, forming the SERS-active sites, and the spectral lines became more intense. The intensity of the SERS bands decreased again, starting at ca. $-300$ mV. The main features of this pyrazinium spectrum in the 1000 cm$^{-1}$ region are the decrease in the intensities of the envelope that contains the 1018 and 1031 cm$^{-1}$ bands and the appearance of a very strong band at 1002 cm$^{-1}$ (Fig. 2A). In the 1200 cm$^{-1}$ region (Fig. 2B) one can also notice the decrease in the 1222 cm$^{-1}$ band and the appearance of a 1200 cm$^{-1}$ band. New bands are not formed in the 1600 cm$^{-1}$ region (Fig. 2C). The 1616 cm$^{-1}$ band intensity just decreases as the potential becomes negative and vanishes completely at $-330$ mV.

The spectral observations at potential values more negative than $-200$ mV suggest that the pyrazinium cation is either tilted or flat-adsorbed on the metallic surface. The bands at 1002 cm$^{-1}$ and at 1200 cm$^{-1}$ can be assigned to the ring modes, numbers 1 and 9a, respectively. The shifts of flat-adsorbed pyrazine ring modes to lower wave number have been observed by Moskovits et al. (17). Similar changes were also observed in the benzene SERS spectrum (16). When aromatic molecules interact with the surface by π-electrons of the ring they adsorb flat. This interaction is expected to shift the ring stretch frequencies downward. The flat-adsorbed benzene SERS spectrum is also completely dominated by the ring breathing mode (number 1) (16). For instance, this mode is several times more intense than the ring stretch mode number 8a, which dominates the spectrum of the end-on adsorbed pyrazine. In Fig. 2, at a potential of ca. $-300$ mV, the 8a mode is hardly observed, but the ring breathing mode is still intense. Another interesting band is at 898 cm$^{-1}$, marked with an asterisk (*) in Fig. 1. This band is assigned to the γ ring mode number 10α (out-of-plane), and it is completely absent in the SERS spectrum of pyrazine (4). However, this band is fairly intense in the benzene spectrum (16) and, following the SERS selection rules, it is expected to be active only for a flat-adsorbed molecule. Similarly, the presence of the 1002 cm$^{-1}$ band (also marked with an asterisk (*) in Fig. 1) is consistent with the flat orientation.

In the potential range where the monoprotonated pyrazine is adsorbed flat, the silver oxidation products, AgBr or (AgBr)$_2^+$, have largely been reduced to metallic silver. This process increases the specific halide surface concentration very significantly. Hence, the flat-adsorbed pyrazinium cation may be bound to the halide layer, which is adsorbed to the positively charged silver surface, as shown in Fig. 4b.

Conclusions

The SERS spectrum of monoprotonated pyrazine was measured. The pyrazinium cation can adsorb onto the electrode surface by two different orientations. The end-on adsorbed monoprotonated pyrazine is predominant at potentials more positive than $-170$ mV. The flat-adsorbed pyrazinium cation is thought to be the only specie on the surface at potentials more negative than $-300$ mV. The positively charged pyrazinium cation must use either the halide or the (AgBr)$_2^{2-}$ complex as a bridge to adsorb to a positive electrode surface.

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References


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