Pyrazine is a centrosymmetric molecule which belongs to the $D_{4h}$ point group. The vibrational selection rules for molecules containing a centre of symmetry include the so-called ‘exclusion principle’. Thus the modes symmetrical to the inversion element (‘$g$-type’) are Raman active, IR forbidden. The vibrational modes antisymmetrical to the inversion centre (‘$u$ type’) are IR active and Raman inactive. The $A_u$ modes are inactive in both Raman and IR. However, when pz is adsorbed on a metal, the metallic surface perturbation can ‘activate’ the forbidden modes.\(^1\) The origin of this perturbation can be either electromagnetic\(^3\) or due to a symmetry lowering provoked by the adsorption.\(^5\) The appearance of forbidden bands in the surface Raman spectrum makes this molecule very attractive for the study of surface selection rules.\(^6\) The presence and the intensities of SERS bands convey important information about the molecular orientation on the electrode surface. Several SERS studies involving adsorption of pyrazine on gold\(^4\) and silver\(^6,7\) electrodes have been reported. In these studies, the role of the metal on the activity and the positions of the bands of the adsorbed pyrazine has been discussed; all reported the presence of pz-forbidden bands.\(^8\) However, a comparison of these reports reveals several controversial aspects. The differences in the spectral features reported by different workers may reflect different experimental procedures and conditions. Several of the controversial bands observed in these SERS studies were assigned to pyrazine’s Raman-forbidden modes, activated by the presence of the surface. However, some of these bands can be assigned to trapped pyrazine decomposition products on the electrode surface, as we have demonstrated in a previous report.\(^9\) These pyrazine decomposition products can be generated electrochemically, when the electrode potential is set to values more negative than $-1000$ mV (vs. SCE) in bromide medium. The reduction of pyrazine is a well known process.\(^10,11\) The main product in this reaction is the 1,4-dihydropyrazine cation (DHPz\(^+\)), as shown in Fig. 1. The cation may undergo subsequent different reactions, such as ring opening, halogenation, and polymerization, depending on the medium and on the electrolysis time.\(^10,11\) In this study, SER spectra from electrochemically-reduced pyrazine are reported. The spectral features are tentatively assigned to the 1,4-dihydropyrazine cation adsorbed onto the bromide-ion-coated silver working electrode. This reduction process is largely irreversible, as indicated by the spectrum.

**Experimental**

**Reagents**

The following chemicals were used without further purification: pyrazine 99+% from Aldrich and KBr AnalR grade from BDH. All solutions were prepared with Milli-Q-water.

**Electrochemistry**

The three-electrode spectroelectrochemical cell has been described elsewhere.\(^1,2\) A potentiostat PAR model 273 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 0.06 µm. 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.

**Activation procedure**

Oxidation–reduction cycles (ORCs) were performed on the silver electrode in an aqueous solution containing 1.0 M KBr and 0.1 M pyrazine, scanning from $-1300$ to $-50$ mV at 5 mV/s for 5 cycles. The electrode was re-oxidized when the potential scan was switched to positive values. This DHPz\(^+\) (or one of its derivatives with similar structure) remained trapped on the electrode surface even at potentials more positive than the point of zero charge (pzc) of silver in this medium. It is proposed that the cation binds to adsorbed halide at potentials more positive than the pzc. The presence of reduced pyrazine products at potentials more positive than the pzc can lead to misinterpretations of the SER spectrum of pyrazine.

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\[ \begin{align*}
\text{pyrazine (pz)} & \quad + 3\text{H}^+ + 2\text{e}^- \\
\rightarrow & \quad \text{dihydropyrazine (DHPz)}
\end{align*} \]

**Fig. 1** Electrochemical equation for pyrazine reduction
The total anodic charge density passed through the system was ca. 60 mC cm\(^{-2}\); this charge was almost all recovered in the cathodic scan. Pyrazine reduction became observable at potentials more negative than ca. \(-1000\) mV.

**Raman spectra**

The Raman spectra were measured with a Dilor OMARS 89 spectrometer with an optical multichannel analyzer (OMA). The intensified diode array (512 diodes) detector was thermoelectrically cooled to ca. \(-10\) °C. The spectrometer was interfaced to an IBM PC-AT 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 a 514.5 nm (100 mW at the head) line from a Coherent Innova 70 argon ion laser, chopped at 1 Hz, as required by the Dilor Spectrometer.

**Results and Discussion**

Fig. 2A and 2B show the cyclic voltammograms obtained for the Ag electrode in 1.0 M KBr medium in the absence and in the presence of pz. Fig. 2A indicates that the presence of pz has some influence on the silver anodic dissolution in this medium. In fact, the oxidation process was less effective for the solution containing the organic molecule, and it can be observed that the presence of pz adsorbed on the silver surface inhibited part of the metallic dissolution process. The electrochemical reduction of pz is shown in Fig. 2B. Pz decomposition occurs simultaneously with hydrogen evolution, and a reduction peak is observed at ca. \(-1250\) mV (vs. SCE). After the electrochemical reduction of pz the potential sweep was switched to the positive direction, and a very weak oxidation peak was observed at ca. \(-1125\) mV (Fig. 2B). This oxidation wave is due to the re-oxidation of the DHPz\(^+\) cation to pz. Analysis of the cyclic voltammogram presented in Fig. 2B suggests that pz’s electrochemical behaviour is not reversible; Thietke et al.\(^6\) reported a reversible electrochemical process for pyrazine reduction in sulfate medium.

Fig. 3, regions 1–4, shows the spectral changes observed as pz was being reduced at potentials more negative than \(-900\) mV. These spectra were obtained after an OCR from \(-1300\) to \(-50\) to \(-1300\) mV at 5 mV s\(^{-1}\); hence, some reduced pz was formed prior to the sweep. All pz characteristic bands either vanished or shifted as the potential was swept in the negative direction, and new bands attributed to pz reduction products were observed. For instance, the SER intensity of the \(\delta\) ring \(6a\) mode at 620 cm\(^{-1}\), due to pyrazine, decreased as the potential became more negative (Fig. 3, region 1), and two new broad bands appeared at ca. 520 and 750 cm\(^{-1}\), respectively. Fig. 3, regions 2 and 3, show the vanishing of the pz bands at 1019 cm\(^{-1}\) (ring breathing mode, number 1), 1220 cm\(^{-1}\) (combination 11 + 16b), and 1235 cm\(^{-1}\) (9a). New bands appeared in those regions at ca. 930 cm\(^{-1}\) and 1175 cm\(^{-1}\). Finally, in Fig. 3, region 4, one can notice the decrease in the 8a- ring pyrazine mode at 1590 cm\(^{-1}\) and the presence of a new band at ca. 1630 cm\(^{-1}\). These new bands are listed in Table 1.

It is not possible to infer the identity of the reduction product from only the Raman frequencies presented in Table 1. However, previous electrochemical work has shown that the main product in the reduction of pyrazine in aqueous medium is DHPz\(^+\).\(^\text{10, 11}\) These authors also predict that DHPz\(^+\) can undergo a homogenous chemical reaction, leading either to ring opening or to ring condensation. These processes are catalysed by hydronium cations, and therefore they are more likely to occur in a very acidic medium (\(\text{pH} < 2\)). This is not the medium used in this work; rather the pH was close to 7. Moreover, the spectral features, presented in Fig. 3 and listed in Table 1, are not compatible with the formation of either an aliphatic or a ring-condensed structure. Another homogeneous chemical process which may also be considered is the halogenation of the DHPz\(^+\), because we work in a concentrated bromide medium. In fact, the band at ca. 520 cm\(^{-1}\) can be assigned either to a C—Br stretch\(^\text{13}\) or a ring deformation. However, as demonstrated later, our SERS results indicate that the species adsorbed on the electrode surface is a cation, and halogenation would probably yield a neutral species.

**Table 1** Vibrational frequencies (cm\(^{-1}\)) and assignments for pyrazine and vibrational frequencies for the product

<table>
<thead>
<tr>
<th>Frequency for pz adsorbed on Ag electrode(^a)</th>
<th>Assignment</th>
<th>Frequency for the electrochemically reduced pz</th>
</tr>
</thead>
<tbody>
<tr>
<td>360vw</td>
<td>(A_1(16a))</td>
<td>295vw</td>
</tr>
<tr>
<td>432w</td>
<td>(B_3(16b))</td>
<td>520w</td>
</tr>
<tr>
<td>630m</td>
<td>(A_1(6a))</td>
<td>620w</td>
</tr>
<tr>
<td>697w</td>
<td>(B_3(6b))</td>
<td>725w</td>
</tr>
<tr>
<td>741w</td>
<td>(B_4(4))</td>
<td>751w</td>
</tr>
<tr>
<td>797w</td>
<td>(B_4(11))</td>
<td></td>
</tr>
<tr>
<td>916vw</td>
<td>(B_1(10a))</td>
<td>906w</td>
</tr>
<tr>
<td>1019s</td>
<td>(A_1(1))</td>
<td>1030m</td>
</tr>
<tr>
<td>1040vw</td>
<td>(B_4(12))</td>
<td></td>
</tr>
<tr>
<td>1116vw</td>
<td>(B_1(18a))</td>
<td></td>
</tr>
<tr>
<td>1215m</td>
<td>(A_1(11 + 16b))</td>
<td>1175m</td>
</tr>
<tr>
<td>1235s</td>
<td>(A_1(9a))</td>
<td></td>
</tr>
<tr>
<td>1324vw</td>
<td>(B_1(3))</td>
<td></td>
</tr>
<tr>
<td>1514w</td>
<td>(B_2(8b))</td>
<td></td>
</tr>
<tr>
<td>1587s</td>
<td>(A_1(8a))</td>
<td>1630s</td>
</tr>
<tr>
<td>3020m</td>
<td>(B_2(7b))</td>
<td></td>
</tr>
<tr>
<td>3030s</td>
<td>(A_1(2))</td>
<td>3060m</td>
</tr>
</tbody>
</table>

\(^a\) From ref. 9. Intensities: v, very; w, weak; s, strong and m, medium.
Fig. 3 SER spectra of pz adsorbed on silver at several potentials. System: Ag/1.0 M KBr/pz 0.1 M. The DHPz\(^+\) bands can be observed at more negative potentials. (a) −900 mV (b) −1000 mV (c) −1100 mV (d) −1200 mV.

Fig. 4 shows the SER spectra of pyrazine in the ca. 1600 cm\(^{-1}\) region at several more positive potentials. Only one band at ca. 1590 cm\(^{-1}\) was observed in this region in the pz SER spectrum presented in ref. 9. However, two bands are observed in Fig. 4 at 1590 and 1610 cm\(^{-1}\). The appearance of these two bands can be explained by the presence of trapped DHPz\(^+\) cation (or structurally similar species), coadsorbed with pz molecules. In order to obtain the spectra presented in Fig. 4, the electrode potential was swept to values more negative than −1000 mV, and the negative potential was applied for sufficient time for the pz reduction to take place. The electrode was then swept to positive potentials; a very weak oxidation wave was observed (voltammogram presented in Fig. 2B), but the presence of a new peak at ca. 1610 cm\(^{-1}\) suggests that some of the reduced pz, which had not been re-oxidized to pz, was either trapped on the electrode surface or in the solution diffusion layer. This is consistent with an irreversible redox process. The electrode potential was again swept in the negative direction commencing from −350 mV and spectra were measured. The integrated intensities from the two bands at 1610 and 1590 cm\(^{-1}\), shown in Fig. 4, were evaluated using band fitting procedures, and are plotted against the applied potential in Fig. 5. It is clear that the 1610 cm\(^{-1}\) band intensity from DHPz\(^+\) decreases and the 1590 cm\(^{-1}\) band intensity from pz increases as the applied potential becomes more negative. The 1610 cm\(^{-1}\) band vanishes at potentials more negative than ca. −700 mV. This band shows up again at ca. 1630 cm\(^{-1}\) when the electrode potential is more negative than −900 mV, as observed in Fig. 3, region 4.

Fig. 5 Integrated SERS intensities of the 1590 cm\(^{-1}\) band of pz (······) and the 1610 cm\(^{-1}\) band of DHPz\(^+\) (———) plotted against potential in the range −1200 to −300 mV.

The presence of bands due to reduced pz in the potential range between $-450$ to $-650$ mV can lead to misinterpretation of the SER spectrum of pz. A comprehensive comparison of the pz bands reported in the literature and the DHPz$^+$ bands has been published elsewhere. The 1590 cm$^{-1}$ band intensity (Fig. 4 and 5) increases as the potential becomes negative, reaches a maximum at $-750$ mV, and then decreases as the potential becomes more negative. This behaviour is common in SER experiments, and is in accordance with other results for pz in the literature. The symmetric profile of the intensity vs. potential plot of the 1590 cm$^{-1}$ band is typical for neutral molecules, and largely reflects the changes in the surface coverage with potential. However, an additional intensity contribution from a resonance process involving the incident light and a charge-transfer between the Fermi level of the metal and the pz LUMO orbital cannot be discounted. The decrease of the 1610 cm$^{-1}$ band intensity as the potential becomes more negative is also consistent with the desorption of a positive ion (possibly as the DHPz$^+\cdot Br^-$ ion-pair from the bromide surface layer cf. ref. 15–17) from the electrode as shown in Fig. 6. The fact that the band at 1610 cm$^{-1}$ only appears after pz reduction at negative potentials is an indication that a cation remains adsorbed on the electrode, even at potentials more positive than the pz (Fig. 5).

The DHPz$^+$ cation is formed at potentials more negative than $-1000$ mV, in the hydrogen-evolution region. However, as the scan is reversed to positive potential, some of the reduced pz compound is re-oxidized to pz (Fig. 2), but some apparently remains as DHPz$^+$ cation (Fig. 4), because pz reduction is an irreversible process. This positive ion is not expected to interact with the silver electrode at potentials more positive than the pz. Hence, no DHPz$^+$ signal is expected in the range of potential between $-450$ mV to $-700$ mV. However, as observed in Fig. 4 and 5, the intensities for the DHPz$^+$ bands are very significant in this range. It is well known from SER experiments on silver electrodes in halide-containing media that a halide layer exists in that potential range, and may partially remain on the electrode surface even at negative potentials. This kind of super-equivalent adsorption has been demonstrated for bromide adsorbed on silver single crystals. Consequently, the DHPz$^+$ cation can interact with the positively charged electrode through the halide layer. As the potential becomes negative, the halide leaves the electrode surface together with the DHPz$^+$ cation and the 1610 cm$^{-1}$ band intensity decreases. The DHPz$^+$ signal can be observed again at potentials more negative than $-900$ mV, because at these potentials the electrode is negatively charged. This behaviour is also in accordance with the results presented by Thietke et al. In their work, they claim that pz reduction is a reversible process. They reach that conclusion because no SER bands due to the DHPz$^+$ were observed at potentials more positive than $-900$ mV. However, they were working in SO$_4^{2−}$ medium; this anion does not adsorb strongly to the silver surface, and hence the DHPz$^+$ cation could not be observed on a positively charged electrode.

It is also important to point out the influence of the porous structure of the rough electrode on the electrochemical kinetics for the pz reduction. The surface morphology for a rough silver electrode prepared from a series of ORCs has been characterized. Fig. 7 shows the time dependence of the cathodic charge for the reduction of pz on both a rough and a

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**Fig. 6** Models of the electrode surface at several potentials. Bromide ions are directly in contact with the electrode surface at potentials more positive than the pz; the DHPz$^+$ cation can adsorb to the halide layer. As the potential becomes more negative, the amount of specifically adsorbed bromide decreases and the DHPz$^+$ Raman signal also decreases. At potentials near the pz, the pz signal maximizes. At potentials more negative than the pz, the DHPz$^+$ cations can interact directly with the electrode surface.

**Fig. 7** Chronocoulometric curves [cathodic charge ($Q_c$) vs. time ($t$)] for the reduction of pz in 1.0 M KBr solution. Potential step from $-700$ to $-1300$ mV. (a) Smooth Ag electrode in the absence of pz; (b) single Ag electrode; [pz] = 0.01 M; (c) roughened Ag electrode (as described in the experimental section); [pz] = 0.05 M; (d) roughened Ag electrode, [pz] = 0.05 m.
smooth silver surface in bromide medium. The results presented in Fig. 7 were obtained by stepping the potential from $-400$ mV, where no faradic process is occurring, to $-1300$ mV, where the reduction of pyrazine is the main contribution to the cathodic current. One can notice that the cathodic charge from a rough surface is at least three times larger than from a smooth surface. The increase in the cathodic charge owing to the surface roughness can be explained by an overall increase in the surface area; however, it has been demonstrated that the surface morphology may affect both the diffusion and the transfer coefficient. The cavities and irregularities present in a rough surface may also trap either pz or its decomposition product. Therefore, for a SERS study, the activation of the silver electrode in the absence of the organic molecule is generally preferable.

**Conclusion**

The electrochemical reduction of pyrazine in bromide medium is irreversible. The main electrochemical reduction product is 1,4-dihydropyrazine cation (DHPz$^+$). Bands due to DHPz$^+$ were observed at potentials more negative than $-900$ mV. The SERS intensities from pz bands decreased as the DHPz$^+$ cation was being formed at negative potentials. DHPz$^+$ was observed at potentials more positive than the pzc for silver in bromide medium (between $-450$ and $-750$ mV), notwithstanding the oxidation wave in the voltammogram. In spite of its positive charge, DHPz$^+$ (or one of its derivatives with similar structure) stays on the electrode surface at potentials more positive than the pzc; the cation interacts with the electrode via the halide layer. Its presence confirms that the electrochemical decomposition of pz is irreversible (it is apparently more difficult to extract protons from the product than to add them). The presence of DHPz$^+$ bands in the pz SER spectrum can complicate the spectral analysis. The contamination of SERS spectra by electrochemically generated products can be avoided by activating the electrode in the absence of the organic molecule.

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**References**


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