

## Surface-Enhanced Raman Spectra of Pyridine and Pyrazine Adsorbed on a Au(210) Single-Crystal Electrode

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Surface-enhanced Raman scattering (SERS) spectra of pyrazine and pyridine adsorbed on an “unroughened” Au(210) electrode surface have been obtained for the first time. The SERS spectra indicate that both pyridine and pyrazine adsorb on the Au(210) electrode via their nitrogen lone pairs (end-on configuration). The integrated SERS intensities from the ring-breathing vibrations (ca. 1010 cm<sup>-1</sup> for pyridine and 1019 cm<sup>-1</sup> for pyrazine) were measured. The potential profiles (integrated SERS intensity versus potential plots) were compared to the surface coverage data, obtained electrochemically, for the adsorption of pyridine and pyrazine on Au(210). No simple relationship was found between the SERS intensities and the surface coverage data; however, it seems that the SERS intensities track the surface coverage for low surface concentrations (less than a monolayer).

### Introduction

The identities and orientations of molecules adsorbed onto electrodes can be obtained by the “in situ” observation of their surface-enhanced Raman scattering (SERS).<sup>1</sup> However, the necessity of creating a rough, and not well-characterized, surface to activate SERS is a major impediment when seeking to correlate SERS intensity with surface coverage obtained from “unroughened” electrode surfaces.<sup>2</sup>

Unenhanced Raman spectra from molecules adsorbed on single-crystal silver in a UHV situation have been reported, but the signal-to-noise ratio was low.<sup>3</sup> Relatively intense electrochemical SERS spectra from pyridine adsorbed on Ag(111) and Ag(100) have been reported<sup>4,5</sup> showing, for each orientation, distinct spectral features as long as the oxidation–reduction cycles (ORCs) used to activate the electrodes were sufficiently weak. We believe, however, that these surfaces have changed even during these mild ORCs, performed in the presence of both halide and the organic molecule. Other techniques to obtain SERS spectra from molecules adsorbed on single crystals have been used.<sup>6,7</sup> For instance, the Raman signal can be improved either by underpotential deposition (UPD) of a monolayer of a SERS substrate onto the single-crystal face<sup>6</sup> or by the direct excitation of the surface plasmons from a flat surface, obtained using a hemispherical prism.<sup>7</sup>

Recently, the signal-to-noise limitation is being overcome. Raman spectra from molecules adsorbed on unroughened surfaces can now be observed due to the advent of a new generation of high-sensitivity Raman spectrometers equipped with CCD detectors. Consequently, both the enhanced and unenhanced Raman spectra from molecules adsorbed on “smooth” surfaces of polycrystalline<sup>8</sup> and single-crystal electrodes<sup>9</sup> have been reported. Using these new systems, it is even possible to obtain Raman spectra from molecules adsorbed on unusual SERS substrates, such as platinum and nickel.<sup>10</sup> Thus the

application of electrochemical Raman spectroscopy can now be extended to the in-situ investigation of a wide range of well-structured interfaces. In fact, surface Raman spectroscopy is a common tool for the study of self-assembled monolayer (SAM) systems.<sup>11,12</sup> Although the SERS intensities may not accurately reflect the amount of adsorbed molecules,<sup>13</sup> one can not deny the importance of electrochemical SERS in the qualitative analysis of the solid–liquid interface (characterization of the structure and orientation of the adsorbed molecules). The comparison of the SERS intensities of pyridine<sup>14</sup> and pyrazine<sup>15</sup> adsorbed on an unroughened gold electrode to the electrochemically-determined surface coverage has been made. These results showed that the SERS intensities track the surface concentration of the adsorbed molecule up to 2/3 of a monolayer. The possibilities brought by the new instruments suggest that these studies, involving the relationship between SERS intensities and surface concentration, can be extended to single-crystal surfaces. The thermodynamic parameters of adsorption, including the surface coverage, for simple organic molecules adsorbed on single-crystal gold electrodes are being measured in our Centre.<sup>16</sup> These electrochemical data can be directly compared to our SERS results.

In this work, the electrochemical SERS spectra of pyridine (py) and pyrazine (pz) adsorbed on an unroughened Au(210) electrode are presented for the first time. Au(210) was the chosen substrate, because this single-crystal surface is very stable, and, unlike other single-crystal faces, it does not undergo reconstruction during potential sweeps. Moreover, the “kinked” surface structure of Au(210) provides a natural “roughness” which might increase the Raman signal. The potential-dependent SERS intensities of pyridine and pyrazine adsorbed on Au (210) were obtained. The SERS intensities were compared to the surface concentrations obtained electrochemically.

### Experimental Section

**Solutions.** All solutions were prepared from Milli-Q water. All SERS experiments were performed in 0.1 M KClO<sub>4</sub> (BDH). The KClO<sub>4</sub> was purified by calcinating at 300 °C, recrystallizing

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twice from Milli-Q water, and then drying. Pyrazine (99+%) from Aldrich and pyridine (analytical grade) from BDH were used without further purification. The solutions were purged with nitrogen for at least  $\frac{1}{2}$  h before taking measurements, and a gentle  $N_2$  stream was kept over the top of the solution during experiments.

**Electrodes.** The Au(210) single-crystal rod (Johnson Matthey, 99.99% pure) was prepared according to the method described elsewhere.<sup>17</sup> A Teflon holder was used. The gold electrode was polished to a mirror finish with progressively finer grades of alumina ending with the 0.3  $\mu\text{m}$  grade. The electrode was cleaned by flaming and quenching with Milli-Q water and transferred to the cell.

The counter electrode was a platinum wire, separated from the working electrode compartment by a porous glass frit. A saturated calomel electrode (SCE) was used as the reference electrode. Therefore, all potentials reported in this work are against the SCE. A Luggin capillary was used to minimize the IR drop.

**Activation Procedure.** *Preparation of an Unroughened Au(210) Electrode.* The unroughened gold electrode was prepared using the technique developed in our previous work.<sup>14</sup> A clean gold electrode was placed in the SERS cell containing 0.1 M  $\text{KClO}_4$  and the desired concentration of adsorbate. The electrode was submitted to continuous cleaning cycles between the limits  $-0.8$  and  $+1.1$  V at 20 mV/s. This cycling persisted until a cyclic voltammogram reproduced itself from one cycle to the next and displayed the features of a clean gold electrode. After the SERS experiments, the electrode was rinsed with copious amounts of Milli-Q water and flame annealed. The electrode was then transferred to a clean electrochemical cell containing 0.1 M  $\text{KClO}_4$  solution. Cyclic voltammograms were obtained in the region between  $-0.8$  and  $+1.1$  V at 20 mV  $\text{s}^{-1}$ . The voltammograms presented features uniquely characteristic of a Au(210) surface.<sup>18</sup> This surface characterization was carried out to confirm that the electrode surface was preserved during the SERS experiment.

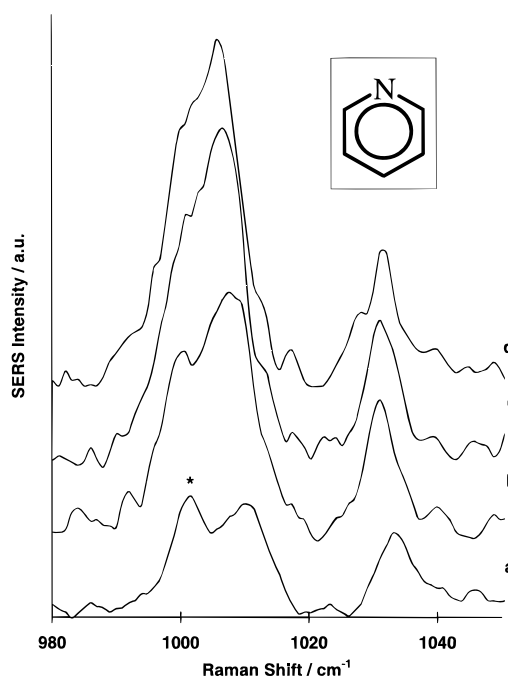
**Instrumentation.** A Renishaw 1000 Raman microscope system equipped with a CCD was used in the SERS experiments. A macropoint accessory, with 40 mm focal length, was used to redirect the laser light to the electrode surface in the spectroelectrochemical cell described elsewhere.<sup>1</sup> A PC computer, interfaced to the spectrometer, contained the data acquisition package with programs for base line correction, smoothing, and band fitting. A potentiostat PAR model 273 was used in the electrochemical and SERS experiments.

A 35 mW Melles Griot He-Ne laser provided excitation at 632.8 nm. The laser power was ca. 6 mW at the sample. The diameter of the laser focus was ca. 5  $\mu\text{m}$ .

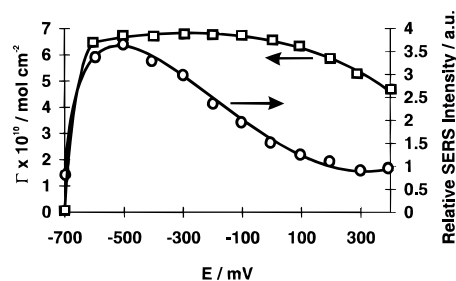
## Results and Discussion

Figure 1 shows the SERS spectra of pyridine adsorbed on Au(210) at several potentials. The band at ca. 1002  $\text{cm}^{-1}$ , marked with an \* in Figure 1, is due to the ring-breathing mode of the aqueous (1 mM) pyridine. The bands at ca. 1010 and ca. 1035  $\text{cm}^{-1}$  correspond to the ring-breathing mode (number 1) and the ring mode (number 12), respectively, for pyridine molecules adsorbed on the single-crystal face. The positions of these two peaks are in good agreement with the adsorption of neutral pyridine on electrode surfaces reported in previous SERS work.<sup>19</sup>

The dependence of both the integrated SERS intensity of the ring-breathing vibration and the surface coverage, for pyridine adsorbed on a Au(210) electrode, on the applied potential are compared in Figure 2. The SERS intensity presented in Figure

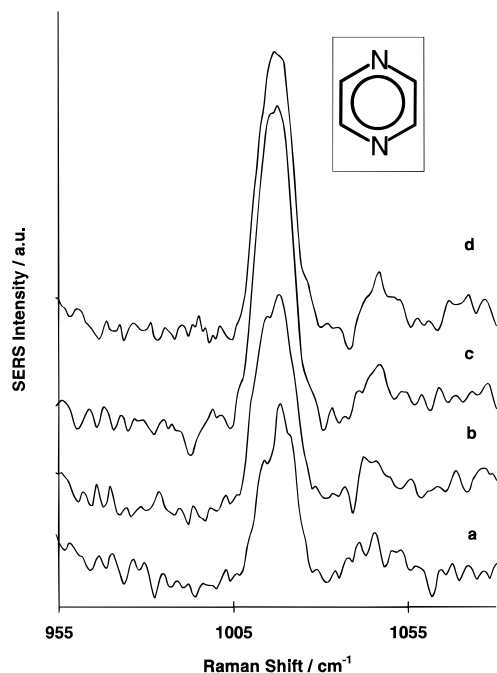


**Figure 1.** SERS spectra of pyridine adsorbed on a Au(210) single crystal at several potentials: (a) +200 mV; (b) -100 mV; (c) -400 mV; (d) -600 mV. (\*) Band from aqueous pyridine. From a 0.1 M  $\text{KClO}_4$  + 1 mM pyridine solution.



**Figure 2.** Dependence of both the integrated SERS intensity and the surface coverage (from ref 18) on the applied potential for pyridine adsorbed on a Au(210) single crystal.

2 was normalized, using the aqueous perchlorate stretch band (ca. 934  $\text{cm}^{-1}$ —not shown in Figure 1) as an internal standard. The SERS potential profile (SERS intensities vs applied potential plot) peaks at ca. -500 mV. This peak is considerably more negative than that observed previously for the SERS of pyridine adsorbed on polycrystalline gold electrodes (-400 mV).<sup>14</sup> The potential-of-zero-charge (pzc) for a Au(210) electrode in 0.1 M  $\text{KClO}_4$  medium has been determined electrochemically.<sup>18</sup> Its value (ca. -100 mV) is more negative than the pzc determined for a polycrystalline gold electrode<sup>20</sup> (ca. -40 mV). Therefore, the shift in the maximum of the SERS potential profile is larger than the shift in the pzc value when these values, obtained for pyridine adsorbed on Au(210), are compared to the pyridine adsorption on Au(Poly). The surface concentration vs applied potential plot (Figure 2) shows that the Au(210) surface is heavily packed in the potential range between -700 and +400 mV. It has been demonstrated that the SERS intensity for molecules adsorbed on a polycrystalline gold electrode tracks the surface coverage only for low surface concentrations (up to  $\frac{2}{3}$  of a monolayer).<sup>14</sup> Therefore, it is difficult to find some simple correlation between the SERS intensity and the surface coverage for pyridine adsorbed on Au(210). The surface concentration of a full monolayer of pyridine on this surface is ca.  $6.7 \times 10^{10}$   $\text{mol} \cdot \text{cm}^{-2}$ . Hence, a relationship between the SERS intensity and the surface coverage is expected

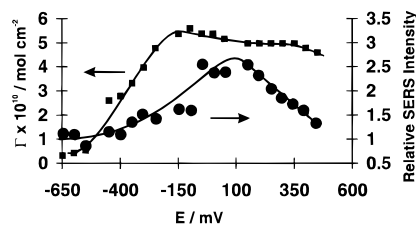


**Figure 3.** SERS spectra of pyrazine adsorbed on a Au(210) single crystal at several potentials: (a)  $-450$  mV; (b)  $-150$  mV; (c)  $+200$  mV; (d)  $+300$  mV.

only for surface concentration values up to  $\text{ca. } 4.0 \times 10^{-10} \text{ mol} \cdot \text{cm}^{-2}$ . This surface concentration value occurs, for this system, in a very limited potential range.

The surface concentration for one monolayer of pyridine, determined electrochemically, indicates that the molecule adsorbs on the electrode via its nitrogen lone pair (end-on orientation).<sup>18</sup> The electrochemical data also show that the orientation is potential independent. This result can be confirmed by the analysis of the spectra presented in Figure 1 and SERS selection rules.<sup>21</sup> The procedure consists of determining the polarizability components of the most enhanced SERS bands. This procedure has been applied to several organic molecules adsorbed on electrode surfaces.<sup>21</sup> For a simple aromatic compound, such as pyridine, the position of the ring-breathing mode can give sufficient information to suggest the orientation. For instance, a flat-adsorbed pyridine would interact with the electrode surface using its  $\pi$ -electrons from the ring. This interaction is expected to decrease the frequency of the ring-breathing mode when compared to the spectrum of the "free" molecule in the liquid state. This behavior is observed in the SERS spectra of flat-adsorbed benzene on silver.<sup>22</sup> The ring-breathing mode of adsorbed benzene occurs at  $982 \text{ cm}^{-1}$ , compared to  $992 \text{ cm}^{-1}$  for liquid benzene. The data presented in Figure 1 show no shift of the ring breathing to low frequencies due to the adsorption. In fact, it is clear from Figure 1 that the frequency for the ring-breathing mode of adsorbed pyridine is higher than that observed for solution. This result strongly suggests that pyridine is adsorbed on the Au(210) electrode in an end-on configuration. Moreover, the peak position does not change significantly with the potential. These SERS observations are in good agreement with the electrochemical results.

Figure 3 shows a portion of the SERS spectrum of pyrazine adsorbed on a Au(210) electrode at several potentials. The SERS spectrum of pyrazine adsorbed on a silver electrode has been extensively studied recently.<sup>23</sup> The peak at  $1019 \text{ cm}^{-1}$  corresponds to pyrazine's ring-breathing vibration. The weak peak at  $\text{ca. } 1030 \text{ cm}^{-1}$  is due to the ring mode number 12. This mode is forbidden in the normal Raman spectrum of pyrazine



**Figure 4.** Dependence of both the integrated SERS intensity and the surface coverage (from ref 24) on the applied potential for pyrazine adsorbed on a Au(210) single-crystal electrode. From a  $0.1 \text{ M KClO}_4 + 1 \text{ mM}$  pyrazine solution.

in solution; it has become active for adsorbed pyrazine due to a field gradient enhancement mechanism.<sup>23</sup>

Figure 4 shows the comparison of the SERS potential profile and the surface coverage data<sup>24</sup> for pz adsorbed on a Au(210) electrode. The maximum in the SERS intensity profile occurs at  $\text{ca. } +100 \text{ mV}$ . This maximum is shifted to negative values when compared to the adsorption of pyrazine on polycrystalline electrodes ( $\text{ca. } +450 \text{ mV}$ <sup>15</sup>). This observation is similar to that previously described for the Au(210)–pyridine system. The shift in the maximum of the potential profile may be induced by a change in the pzc. As we observed for the adsorption of pyridine, the surface coverage vs potential curve (Figure 4) indicates that the Au(210) surface seems to be saturated with pyrazine in a wide potential range. However, in this case, there is a more gentle rise in the surface coverage curve in the range between  $-650$  and  $-150 \text{ mV}$ . In this region, where the surface coverage value is a fraction of one monolayer, it seems that there is a correlation between the SERS intensity and the surface coverage; both surface coverage and SERS intensity increase as the potential becomes more positive.

The maximum in the surface coverage curve for pyrazine adsorbed on Au (210), determined electrochemically,<sup>24</sup> is around  $6.0 \times 10^{-10} \text{ mol cm}^{-2}$ . Considering the area occupied by a vertically-oriented pyrazine molecule ( $\text{ca. } 0.25 \text{ nm}^2$ ), this value is consistent with an end-on adsorbed pyrazine. The same argument used earlier to discuss the orientation of the pyridine molecule can be applied here. Raman spectra of aqueous pyrazine solutions<sup>25</sup> show the ring-breathing mode at  $1015 \text{ cm}^{-1}$ . The position for adsorbed pz,  $1019 \text{ cm}^{-1}$ , is higher, consistent with an end-on orientation. Moreover, the general features of the SERS spectrum of pyrazine adsorbed on Au(210) resemble the spectra of pyrazine adsorbed on silver, which strongly suggested an end-on adsorption.<sup>23</sup> Therefore, the electrochemically-determined orientation of pyrazine on Au(210) is confirmed by our SERS results.

Finally, it is important to point out that the absolute signal for the spectra presented here is very low. In fact, the spectra from Figure 3 are  $\text{ca. } 1000$  times weaker than for pyrazine adsorbed on a rough silver electrode in halide medium and, at least,  $100$  times weaker than the SERS spectrum of pyrazine adsorbed on a rough polycrystalline gold electrode. However, the spectra shown in Figures 1 and 3 can be obtained with a reasonable signal-to-noise ratio. Therefore, the advent of the new generation of Raman instruments equipped with CCD detectors opens a new window of possibilities for the study of SERS spectra of molecules adsorbed on single-crystal electrodes.

## Conclusions

Raman spectra from molecules adsorbed on "unroughened" single-crystal electrodes can now be obtained using the new generation of Raman spectrometers equipped with CCD detectors. SERS spectra of pyridine and pyrazine adsorbed on an unroughened Au(210) electrode have been obtained for the first

time with a reasonable signal-to-noise ratio. From the analysis of the SERS spectrum, it is possible to infer that both pyridine and pyrazine adsorb on the electrode surface using the nitrogen lone pair, in an end-on configuration. This result is in good agreement with previous electrochemical data. The SERS intensities have been compared to electrochemically-determined surface concentrations for both species adsorbed on Au(210). No simple relationship between the SERS intensity and the surface coverage has been found for surface concentrations close to one monolayer. However, the SERS intensity seems to follow the surface coverage for low surface concentrations.

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