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# Adsorption of pyrazine on Au(111) and Ag(111): on the role of the electronic factor

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## Abstract

XPS and AES investigations of the emersed Au(111) and Ag(111) electrodes have revealed that pyrazine is more weakly adsorbed on Ag than on Au. Whereas on Au, pyrazine is firmly bound on the surface and the increase in the positive charge of the electrode brings about the increase in the organic surface excess by changing the molecule orientation from a flat to a vertical position being then involved in the subsequent anodic oxidation processes, its bond with silver is so weak that anions remove it easily from the surface. The different behavior of the two electrodes to the pyrazine adsorption has been explained in terms of electronic interactions.

**Keywords:** Auger electron spectroscopy; Chemisorption; Gold; Low index single crystal surfaces; Models of surface chemical reactions; Pyrazine; Silver; Solid–liquid interfaces X-ray photoelectron spectroscopy

## 1. Introduction

There is general agreement that adsorption of organic compounds at electrode/solution interfaces is governed by the competition between the forces involved in the metal solvent and metal–solute interactions. The role of the electronic factor, important in any adsorption phenomenon, is expected to be in this case more complex as for the metal/gas interfaces not only due to the additional interaction with the solvent but also because the electric field may considerably influence the metal as well as the adsorbate electronic states entailing significant changes in the adsorption energetics. It is the case of the

pyrazine adsorption on Ag(111) and Au(111) electrodes that illustrates well the complexity of the electronic factor action in such circumstances and the aim of this paper to discuss it in detail.

Pyrazine is a planar molecule of  $D_{2h}$  symmetry [1] without permanent dipole moment. The adsorption position of such a molecule on the electrode surface is expected to be flat, as observed in the gas phase studies [2–4], and independent on the surface charge unless a specific (electron) interaction occurs. Pyrazine has been reported to be indeed flat adsorbed on Hg [5], in contrast with pyridine, the orientation of which was found to be a function of the electrode potential [5,6]. When it is adsorbed on Au(111), however, this molecule has been observed in the chronocoulometric experiments [7] to change its orientation at the point of zero charge too. Recent XPS and AES investigations of the emersed electrodes performed in our laboratory [8] have pointed

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out the same behavior for the pyrazine adsorbed on Au(111) while at the Ag(111) surface, only one adsorption state could be detected, under the same circumstances. Such an influence of the metal nature as well as the orientation transition of the molecule adsorbed on the Au(111) electrode that cannot be explained anymore in terms of intermolecular H bonding with water in the interphase region [5] or dipole-field interactions [7] invoked in the case of pyridine adsorption on Hg and Au, respectively, suggests a specific interaction of pyrazine with the gold electrode in which the electronic factors play a decisive role.

## 2. Experimental

The XPS and AES investigations were performed on electrodes emersed dry from the electrolyte (after a waiting of 3 min at every potential value) and transferred to the UHV chamber without any other treatment. They have been subjected to several cycles of sputtering/annealing until the surface appeared clean and well ordered in AES and LEED tests prior to each experiment. The XPS data were acquired using unmonochromatized Al K  $\alpha$  radiation with a fixed pass energy of 25 eV. The AES spectra were collected with a primary energy of 2000 eV, a beam current of 10  $\mu$ A and a modulation voltage of 10 V peak-to-peak. The experimental set-up has been previously [9] described and the other details are reported elsewhere [8].

## 3. Adsorption states of pyrazine on Au(111) and Ag(111) electrodes

The XPS and AES investigations on the electrodes emersed at various potential values in the double layer region from 10mM pyrazine in 5mM NaClO<sub>4</sub> solutions revealed [8] a peculiar behavior of the Au(111) and Ag(111) surfaces in the adsorption process of this organic compound. The surface excess of pyrazine was observed to undergo differently the influence of the electrode charge depending on the metal nature. As seen in Fig. 1, although the relative intensities of N 1s and N KLL signals increased with charge for both electrodes at  $E > E_{\sigma=0}$ ,

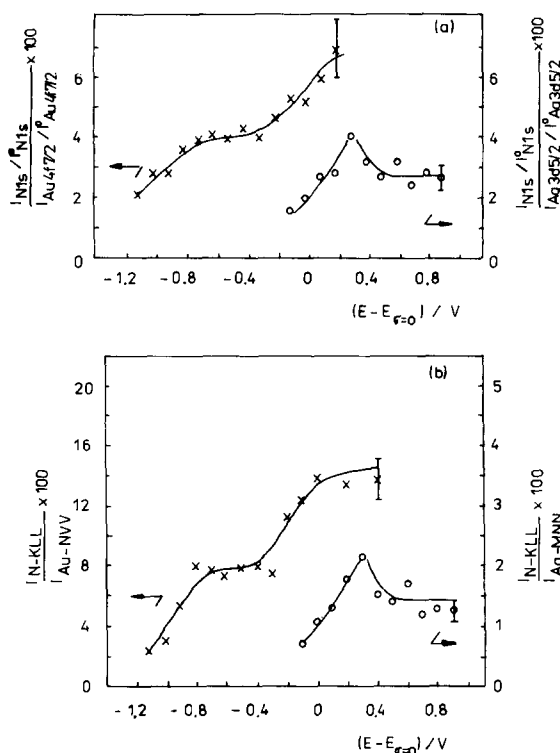


Fig. 1. N 1s (a) and N KLL (b) normalized signals versus the emersion potential,  $E$ , for Au(111) (x) and Ag(111) (o) electrodes (potential values are on a rational scale, i.e. zero for each metal corresponds to  $E_{\sigma=0}$  in the base electrolyte).

the interaction of pyrazine with each metal was distinct. The adsorbed pyrazine reached a constant surface concentration and proved to be strongly held on the Au(111) as the further anodic oxidation of the metal was noticed to be considerably disturbed, but it appeared only weakly bound to the Ag(111) surface being easily replaced by perchlorate anions [8]. At the negatively charged surfaces, the adsorbed pyrazine exhibited a constant concentration over a rather large range of potential values for Au(111) but it was observed to take part in a faradaic process of cathodic reduction on Ag(111), as soon as  $E$  becomes negative to  $E_{\sigma=0}$  [8].

The details on the adsorption states of pyrazine derived from the N 1s core-level binding energies,  $E_B$ , plotted in Fig. 2, pointed out the differences between the two electrodes too. The higher values of this parameter for the pyrazine adsorbed on Ag(111) in a potential region where the electric field effects

should be the same, mean according to Brundle [10], a lower heat of adsorption and hence, a weaker adsorption bond. Besides, the electrochemical shift effect, always observed at the emersed electrodes [11,12], revealed the presence of two adsorbed species at the Au(111) surface by the two distinct slopes depending on the potential region but only one at Ag(111). The higher shift of the binding energy, of 1 eV/V, noticed for the positively charged Au(111) surface, suggests a closer approach of the nitrogen-end of the molecule to the electrode surface and hence, a vertical position, while the lower one, of 0.3 eV/V, observed for the negatively charged Au(111) surface, which is the same with that exhibited by the positively charged Ag(111) electrode, indicates a larger distance to the metal surface and thus, a flat position. Such assumptions, which are in a very good agreement with the results of the chronocoulometry measurements reported by Lipkowski and Stolberg [7] for pyrazine adsorbed on Au(111), have a good support in the values of the full width at the half maximum (FWHM) of the nitrogen XPS signal. As seen in Fig. 3, this parameter has a constant and relatively low value for the species considered to be flat adsorbed and a distinct higher value for that supposed vertically adsorbed, as a consequence of the overlapping XPS signals furnished by the two nitrogen atoms which are non-

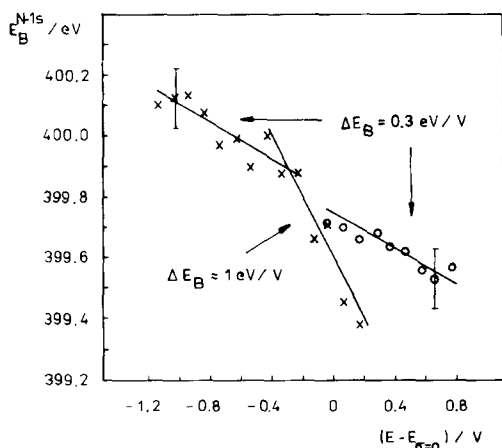


Fig. 2. Electron binding energy for N1s core level,  $E_B^{N1s}$ , as a function of emersion potential,  $E$ , for Au(111) (×) and Ag(111) (○) electrodes.

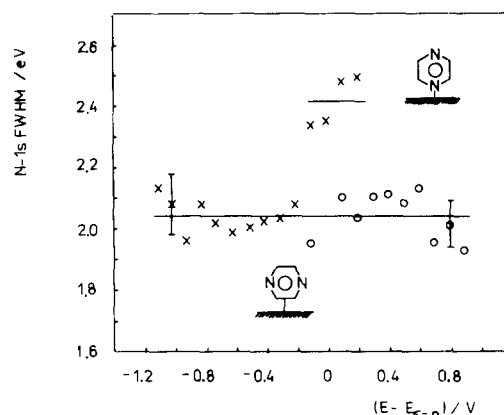


Fig. 3. Full width at half maximum (FWHM) of N1s signal as a function of emersion potential,  $E$ , for Au(111) (×) and Ag(111) (○) electrodes.

equivalent energetically for this molecular orientation. A similar effect has been previously mentioned in the case of the molecular oxygen vertically adsorbed on Ag(111) by Campbell [13].

It follows that pyrazine is not only more strongly adsorbed on Au(111) but its interaction with this electrode is also more complex, yielding two distinct adsorbed species depending on the nature of the surface charge. The interaction with Ag(111) produces only a weakly adsorbed species at potentials higher than  $E_{\sigma=0}$  but gives instead rise to a faradaic process at negative polarizations of the electrode.

The organic adsorption takes place preferentially at  $E_{\sigma=0}$ , when  $H_2O$  is most weakly adsorbed to the metal surface. Trasatti [14] has shown that if no specific adsorbate–metal interaction occurs, the higher the energy necessary to desorb the water molecules from the electrode surface, the weaker the tendency of the organic substances to be adsorbed. It is, therefore, useful to examine firstly the information on the interaction of water with the two electrodes under discussion in order to find out the origin of their different behavior to the pyrazine adsorption.

#### 4. Adsorption of water on Ag(111) and Au(111) electrodes

The UHV studies of water adsorption on metal surfaces have shown that the process is a resultant of

the cohesive and adhesive forces operating between the water molecules and between the water molecules and the metal surface, respectively. Thiel and Madey [15] reported a significant influence of the structural mismatch between the metal substrate and the crystalline ice (found to be representative for the molecularly adsorbed  $\text{H}_2\text{O}$  layer structure) on the strength of the water–metal bond. A weak interaction was predicted when the lattice mismatch was more than  $\pm 0.2 \text{ \AA}$ , as it has been shown to be for the Ag and Au case [15], in very good agreement with the experimental results. Water desorption was observed at about 150–170 K for both silver [16,17] and gold [18], temperatures commonly assigned to bulk ice desorption, which reflects the bond formation parallel to the surface and the almost exclusive action of the cohesive forces in the adsorption layer.

Interaction of water with Ag(111) and Au(111) surfaces is, however, more specific at the electrode/solution interface. The value of  $E_{\sigma=0}$  for Ag(111) ( $-695 \text{ mV}$  versus SCE [19]) is by about 1 V more negative than that of Au(111) ( $285 \text{ mV}$  versus SCE [20]) although the difference in their work functions is only  $0.57 \text{ eV}$ , suggesting a stronger interaction of water with the first electrode. The potential of zero charge,  $E_{\sigma=0}$ , was shown [21] to have a close relationship with the metal work function,  $\varphi$ :

$$E_{\sigma=0}(hkl) = \varphi(hkl) + X(hkl) + \text{const.}, \quad (1)$$

in which an important role is played by the so-called “interfacial parameter”,  $X$ , introduced by Trasatti [22]. The interfacial parameter gives a measure of the interaction between the metal and the water by summing up the contributions of the change in the surface potential of the metal,  $\delta\chi^M$ , due to the contact with solution, and that of the surface potential brought in by the liquid phase,  $g^s(\text{dip})$ ,

$$X(hkl) = \delta\chi^M(hkl) + g^s(\text{dip}). \quad (2)$$

The relative values estimated by Trasatti [22] from the plots of  $\varphi$  versus  $E_{\sigma=0}$  taking Hg as reference pointed out that  $X_{\text{Ag}(111)}$  ( $0.20 \pm 0.01$ ) is about twice the value of  $X_{\text{Au}(111)}$  ( $0.13 \pm 0.02$ ). It has been claimed [21] that only the second contribution of  $X$ ,  $g^s(\text{dip})$ , resulted from the orientation of

the water dipoles depends on the metal nature. The experimental observation that the difference in  $E_{\sigma=0}$  equals the difference in work function for several metals in molten salts [23] is indeed a strong argument in this respect but the surface dipoles resulted in the relaxation of the electron charge density of the metal into the double layer space are dependent on the effective dielectric constant of the bonding phase and hence, function of the dipole orientation degree too in case of water. Therefore, such a conclusion should be taken reservedly. However, whatever the weights of the two contributions are, the origin of the distinct values of the interfacial parameter for Ag(111) and Au(111) is, nevertheless, the orientation of the water molecules.

Water bonds always through the oxygen atom to the surface [15] but the dipole vector pointed from the oxygen end to the hydrogen atoms may adopt a parallel or a more or less vertical position against the surface. Considering that the electronegativity of the metal play an important role in this respect, Trasatti [21] estimated that the degree of the water orientation on gold is zero. Hence, if the water dipole lies parallel to the Au surface, then the higher value of the interfacial parameter of the Ag(111) surface has to be the result of a rather vertical position of it.

A higher value of the interfacial parameter,  $X$ , does not mean, however, necessarily a stronger adsorption bond for water, since  $X$  accounts only for the additional potential drop brought about by the dipole–field interaction at the metal/solution interface. This is particularly the case of the metals under discussion. The observation of empty surface states, an intrinsic property of clean surfaces, at the silver and gold single crystals in contact with aqueous solutions of NaF [24] evidenced that the structure of the double layer water at these two metals is governed by the water–water and water–ion interactions rather than the direct interaction between water and metal [25] as observed at the metal/gas interface too. The same surface states were shown to be attenuated or even completely quenched, depending on the strength of interaction, by the anion adsorption [26]. That Ag(111) and Au(111) electrodes interact differently with pyrazine despite their common weak affinity for water is a good indication, as it has been already stated [14], that determinant for their interfacial properties are the electronic factors.

## 5. Electronic factors involved in the adsorption phenomena at Ag(111) and Au(111) electrodes

The photoemission studies [27,28] agree well with the theoretical approaches [29] in stating that silver and gold bulk electron structures differ mainly by the width and the location in energy of the d-bands. The d-electron states ranging on 5.24 eV for Au [27] and 3.5 eV for Ag [28] are located at about 2 eV under the Fermi level for Au [27] and 4 eV for Ag [28]. The angular-resolved energy distributions for the photoelectrons emitted from the Ag(111) [30] and Au(111) [31] surfaces revealed an additional feature located near the Fermi level in both cases ascribed to an occupied surface state as the only significant contribution of the single crystalline surface.

The gas-phase photoelectron spectrum of pyrazine [32] exhibits, on the other hand, four bands at  $-9.63$ ,  $-10.18$ ,  $-11.35$  and  $-11.77$  eV, assigned in order to the  $a_g(n+)$ ,  $b_{1g}(\pi)$ ,  $b_{1u}(n-)$  and  $b_{2g}(\pi)$  orbitals of the molecule while that of water [33] is characterized by the presence of the  $1b_1(n)$ ,  $3a_1(n)$  and  $1b_2(\pi)$  occupied orbitals with  $-12.6$ ,  $-14.7$  and  $-18.5$  eV, respectively. By inverse photoemission measurements, the lowest unoccupied molecular orbital of pyrazine (LUMO),  $b_{3u}(\pi^*)$ , was found at 0.65 eV under the vacuum level [3].

A schematic plot of the main parameters of the Ag(111) and Au(111) band structure along with the most important molecular orbitals of water and pyrazine for an electron interaction is shown in Fig. 4. Since the geometry of the molecular orbitals is equally important for the adsorbate–surface bonding, the highest occupied molecular orbitals (HOMO) of water and pyrazine as well as the pyrazine's LUMO, considered to be significant for a chemisorption process, are also added in the canonical forms depicted by Jorgensen and Salem [34].

In discussing the chemisorption processes taking place at the metal/gas interface, the simplest model is that in which the surface–adsorbate interaction is considered in terms of simple Lewis acid–base chemistry [35]. Both adsorbed water and pyrazine acting usually as electron donors are considered Lewis bases [15,36] whereas the metal is the electron acceptor. The calculations with metal clusters indicate that bonding of such molecules is mainly due to the participation of the lone pair orbitals of oxygen

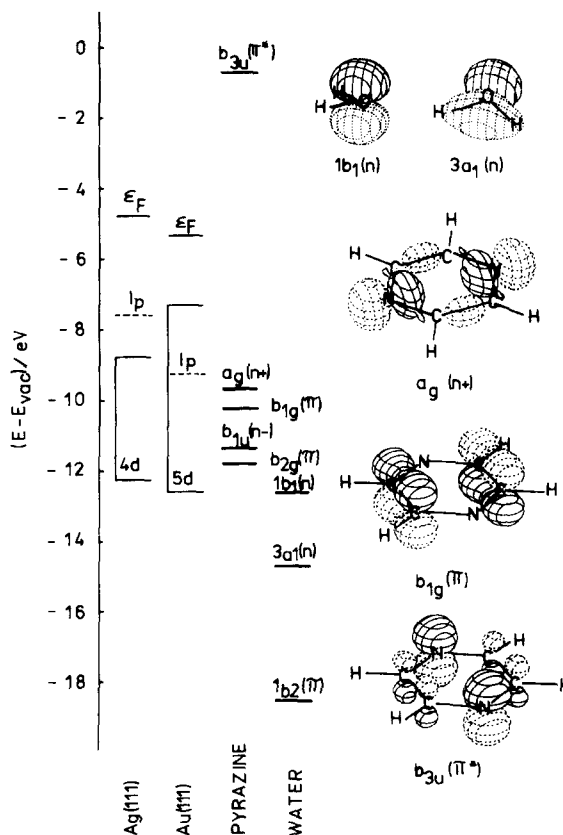


Fig. 4. Schematic plot of the band structure of Ag(111) and Au(111) electrodes and molecular orbitals of pyrazine and water of potential significance in a chemisorption bond (for details, see the text);  $I_p$  values represent the ionization energies for Ag and Au atoms.

in water [37] and nitrogen in azabenzens [38]. The formation of a chemisorption bond involves the mixing of the adsorbate orbitals with the electronic states of the metal, for which similar electron energies and adequate symmetries are required. Taking into account the possible adsorption geometries and the molecular orbitals of  $H_2O$  available for adsorption, the theoretical approaches [39,40] recommend an on-top tilted (dipole parallel to surface) and a bridge-site perpendicular (dipole vertical to surface) orientations as the most favorable ones. According to the spatial distribution of the canonical orbitals of water shown in Fig. 4 and the adsorption geometries predicted by the interfacial parameter values, its bonding at  $E_{\sigma=0}$  should occur through the  $3a_1$  orbital on Ag(111) and the  $1b_1$  orbital on Au(111).

Examining the corresponding orbital energies, it can be easily seen that a hybridization of these two orbitals with the electron states of the two electrodes is hardly probable for Ag(111) and could involve only the full d-band of Au. The participation of the d-bands completely occupied to such a bond has, however, no contribution to its strength, due to the cancellation between the bonding and antibonding counterparts [38]. It is the reason for which these single crystals have in aqueous solutions [24,25] a behavior typical for the clean surfaces as mentioned before. We may conclude, therefore, that at  $E_{\sigma=0}$ , water can be removed from both the Ag(111) and Au(111) surfaces with the same facility. It must be the specific interaction of the organic molecule with the two electrodes that is responsible for the different behavior observed.

The formation of a chemisorbed bond of azabenzenes seems to be in a close interdependence with the adsorption geometry. The angle-resolved photoelectron spectra revealed strong evidence for the mixing of the Ag 4d band and the nitrogen lone pair orbital in case of the vertically adsorbed pyridine on Ag(111) [41] but indicated only a relaxation of the molecular orbitals for the flat adsorbed pyrazine on the same substrate [4]. As the nitrogen lone pair orbitals have practically the same energy in pyrazine (9.63 eV) and pyridine (9.66 eV) [32], it is obvious that only the interaction of the permanent dipole moment of pyridine with the surface dipoles of the metal surface orientating the nitrogen-end of the molecule towards the surface is responsible for the mixing between the metal and organic electron states. For a molecule without permanent dipole moment, the energetic factors are, however, decisive for the formation of a chemisorption bond and the adsorbate orientation is only a consequence of the geometry of the orbitals involved in. The observation that pyrazine adsorbed on nickel has a rather vertical position while the pyrazine condensed on the same surface exhibits an amorphous distribution of molecular orientations [42] is conclusive.

The highest occupied molecular orbital of pyrazine,  $a_g(n+)$ , is compatible energetically with the d-bands of the two electrodes under discussion. The participation of the full d-bands cannot, however, yield an effective chemisorption bond, as mentioned before. The surface excess of this organic molecule

at  $E_{\sigma=0}$  resulted most probably in the solution tendency of lowering its surface tension should be, therefore, weakly bound as in case of adsorption from the gas phase [2,43,44]. Consequently, the water or the anions should be successful in the competition for the surface sites as soon as the electrode charge grows up. However, except for the positively charged silver surface, this does not happen. The specific phenomena observed pleads, thus, for an electron interaction between pyrazine and the electrodes under discussion favored by the action of the electric field on the electron energy levels at both sides of the interface.

The high affinity for electron of pyrazine, pointed out by the low value of its LUMO and its property to form a rather stable negative ion in aqueous solutions reported by Nenner and Schulz [45] is undoubtedly responsible for the phenomena that take place on the negatively charged Ag(111) and Au(111) electrodes. At the gas phase contact or at  $E_{\sigma=0}$ , the difference between the Fermi level and the pyrazine's LUMO is still large for both electrodes to allow an electron interaction, in spite of the fact that the Coulomb relaxation effects may bring them closer. Both an increase of 1.4 eV of the Ag(111) Fermi level [3] and a decrease of the same value of the pyrazine affinity level [44] have been reported in the gas phase studies of this adsorption process. At the electrode/solution interface, however, the field effects known to raise the metal Fermi level as well as to push down the electron levels of the adsorbate, may create favorable conditions for an electron transfer from metal to pyrazine. Such a process is thought to be responsible for the formation of a negative ion that leaves the surface, giving rise to the faradaic process in case of Ag(111) and the decrease of the pyrazine surface concentration, in case of Au(111). The reason for which this process is not a faradaic one in Au(111) case has to be related with the position of the Fermi level. At the higher negative polarization required by the lower Fermi level of Au(111) surface, the interaction of the water dipoles with the electrode is certainly prevailing and hinders the access of the bulk pyrazine to the metal surface limiting the process to the surface species only. It is worth pointing out that the difference of the potentials on the rational scale at which pyrazine starts to be removed from the surface of these two electrodes

(0.6 V) is practically the same as that of their work functions (0.57 eV). The same observation is valid for the reduction of pyrazine on Hg, where under similar conditions, the process was found to occur at 0.53 V negative to  $E_{\sigma=0}$  [46]. Again the difference of the above-mentioned potentials (0.23 V) is similar with the difference in work function (0.25 eV). It is clear that the position of the Fermi level is determinant for the potential value at which the cathodic reduction of pyrazine starts and hence, for the specific conditions under which such a process is developed.

Examining now the situation at the positively charged surfaces, it may be seen that the strong chemisorption of pyrazine on Au(111) cannot be explained anymore by the band structure of the metal. The fully occupied 5d band cannot be taken into account for the reasons mentioned before and a simple comparison of the pyrazine's HOMO ( $-9.63$  eV) with  $\epsilon_F^{\text{Au}}$  ( $-5.31$  eV [47]) shows that the mixing of the conduction band of the Au(111) with the lone pair orbital of pyrazine is not energetically possible. Their difference in energy is too high to be compensated by field effects (shifting  $\epsilon_F$  downwards with 1 eV/V [48] and  $\epsilon(a_g)$  upwards with 1 eV/V – see Fig. 2) or the Coulomb relaxation effects (shifting  $\epsilon(a_g)$  upwards by 0.6 eV [4]) observed at the adsorption from the gas phase. It is obvious that the band structure of the Au(111) surface does not account for the electronic properties of the surface atoms involved in the specific interaction under discussion. Since the half-empty 6s orbital of the gold atom with an ionization potential of 9.22 eV [47] is much more appropriate to form such a bond we may conclude that the *atomic* rather than the *bulk metal* electron states represent properly the surface atoms in this interaction. The formation of the chemisorption bond brings the molecule to a vertical position, the only one optimum for the orbital mixing. Unlike gold, silver has not only a smaller ionization potential (7.57 V [47]) but also, according to its standard electrode potential ( $E_0^{\text{Ag}} = 0.7998$  V;  $E_0^{\text{Au}} = 1.68$  V [47]), a higher tendency to pass into ionic form. For that reason, the silver dissolution takes place before the field effects are able to bring the electron states in metal and pyrazine at the same energy level.

Treating the surface atoms of the metals as isolated species in their interaction with the adsorbate is

commonly used in the studies on gas phase adsorption and catalysis. Calculations of the adsorbate–adsorbent interactions indicate that the most appropriate model to describe a specific system depends on the strength of this interaction. It is generally admitted [35] that if the adsorbate–solid interaction is weak, an electron band (delocalized) model is best and if this interaction is strong, the surface molecule (localized) model is preferred. So, while in the rigid band model, the adsorbate is viewed as a simple electron acceptor or donor which removes or donates an electron in the band of the solid, in the surface molecule description the adsorbate is assumed to interact with one or two substrate atoms forming bonds according to a molecular orbital theory or other chemical binding approach, without invoking the band characteristics at all. Besides, the metal/solution interface is the site of extremely high electric field and it is known that its perturbing action is screened within the first atomic layer due to the high density of electrons near the surface [49]. The electro-reflectance measurements [49] have already proved that the band structure of the bulk cannot not be a proper description for the electron states of the surface atoms that experiences in plenty the local electrostatic potential and the phenomena involving directly these atoms hardly explained by a delocalized model. The failure of the free-electron model to represent many important effects (like the marked influence of the crystallographic orientation) in such measurements, that showed that the bound electrons have to be taken into account in explaining the behavior of the surface atoms is such an example.

It would be certainly premature to draw a general conclusion concerning the nature of the electronic factors involved in the interfacial phenomena at the contact of the metal electrode with the aqueous solutions. However, the participation of the conduction electrons more easily bound to the reduction phenomena and the implication of the surface atoms in chemisorption processes, for the electron states of which the individual orbitals rather than the band structure seem to be a more suited description, does make sense. Only a careful analysis of the role played by the electronic factors in other systems may prove if the examples discussed here are or are not representative. There is no doubt, however, that the

field effects on the electron states at both sides of the interface are decisive for developing specific interactions with organic compounds in aqueous solutions.

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