Proving the Dual Electronic Structure of Charged Metal-Molecule Interfaces: SERS of Cyanide Adsorbed on a Nanostructured Silver Electrode

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ABSTRACT

Experimental and theoretical calculations confirm, for the first time, the existence of two different kinds of electronic structures of a surface complex formed by a particular molecule bonded to charged metal electrodes, clusters or nanoparticles. Surface-enhanced Raman scattering of cyanine adsorbed on a silver electrode shows three regions which are selected by the electrode potential and characterized by the differentiated response of the vibrational wavenumbers of the ν(CN) stretching band to the electrode potential. The combination between experimental SERS and DFT calculations has allowed for relating the three regions to chemisorbed (C-hybrid) and physisorbed (P-hybrid) surface complexes, where cyanide is bonded through the carbon on top of a single silver atom of the surface, and to bidentate species, respectively. The electrode potential selects one or another type of electronic structure of the surface complex which are of different nature and with a differentiated response to the applied potential. Electric potential tunes smoothly the wavenumbers, bond energies and injected charges of the P-hybrid at more negative potentials than that of the zero charge of the electrode, but the very strong C-hybrid prevent significant changes of these properties at positive excesses of charge. The existence of the dual electronic structure of metal-molecule interfaces might require to reinterpret experiments that are usually discussed by resorting to, for instance, the reorientation of the adsorbate, the formation of complexes with different stoichiometry, the existence of nonequivalent local sites on the surface or to instrumental artifacts.

INTRODUCTION

This work shows the existence of two kinds of electronic structures of the hybrid systems formed by a molecule (A) bonded to large charged metals (M) such as organic molecules adsorbed on nanostructured electrodes, metallic clusters, nanoparticles, or located at the tip of an STM instrument or in a molecular junction. Experimental and theoretical results point to a dual electronic structure of a metal-adsorbate (M-A) complex of different nature, being selected one or another by the sign of the density of charge of the metal. The properties of each one of them can be smoothly tuned in a different way by the amount of the positive or negative density of charge of the metal, respectively, but a qualitative change is observed when the sign of the excess of the metal charge is reversed. The existence of two different electronic structures in a charged metal-adsorbate (M-A) surface complex has been predicted[1] on the basis of density functional theory (DFT) calculations of the isonicotinate anion (In^-) adsorbed on an atomistic model of a charged silver electrode/nanoparticle,[2] where the molecule is bonded to the terminal atom of linear metal clusters $[Ag_n]^q$ with different sizes (n) and charges (q) (Figure 1). This prediction is confirmed for the first time in this work by studying the experimental dependence of the vibrational wavenumbers of cyanide adsorbed on a nanostructured silver electrode.

The different length of the $[M_n^q$-A] complexes (Figure 1) allows for defining the averaged density of charge of the metallic clusters as $q_{eff}=q/n$, which quantifies the fractionary charge of a particular atomic site of the surface of a macroscopic electrode, nanoparticle or metallic tip. This effective charge of the clusters ranges from $q_{eff}=+0.33$ to -0.33 a.u. in the stick-like closed-shell

$[Ag_n]^q$ clusters for the extreme cases with n=3 and q=+1 or -1 a.u., respectively, and models the surface excess of charge of the metal which can be experimentally controlled by a potentiostate.[2]

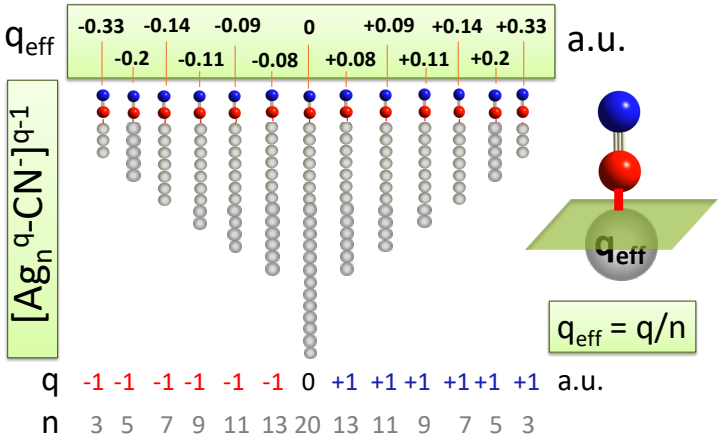

Figure 1. Structures of linear silver-cyanide complexes $[Ag_n^{q}\text{-}CN]^{q-1}$ with different sizes (n) and charges (q=+1, 0 and -1 a.u.) used in the theoretical calculations. The combined variable $q_{eff}=q/n$ models the change of the excess of charge of a surface atom of the electrode under applied voltage.

In the case of isonicotinate ion, $[Ag_n^{q}\text{-}In^{-}]^{q-1}$ hybrids forms strong M-A complexes (chemisorbed, C-hybrid) when silver is positively charged ($q_{eff}>0$) and weak complexes (physisorbed, P-hybrid) at neutral or negative charges ($q_{eff}\leq 0$). This is the expected behavior by considering simple electrostatic interactions when M and A are both charged species, but the electronic structure of a molecule or supermolecule is not exclusively determined by simple electrostatic factors. Previous results[1] conveyed the idea that the C- and P-hybrids, which only differ in the opposite sign of the charge of the metal, correspond to two differentiated chemical systems with the same composition and geometry: They are two surface states, selected by the

electrode potential, of the same complex but of different nature and with sharply differentiated properties. DFT calculations point to a qualitative change in the properties of the M-A complex when the metal has positive or negative charge in both the ground (S_0) and excited (S_i) electronic states like metal-molecule charge transfer states. This means that the electrode potential selects one or other type of electronic structure which controls, for instance, redox reactions in electrochemical interfaces or the electron transport through molecular junctions. The existence of the dual electronic structure of the M-A hybrids could be the cause of the bimodal behavior sometimes observed in particular experiments, but it is very difficult to prove it given that promising experimental results are usually analyzed on the basis of others more classical and widely assumed causes like the hypothetical reorientation of the adsorbate[3] induced by the potential, for instance.

Surface-enhanced Raman spectra (SERS) is a powerful experimental technique able to provide information on metal-adsorbate interfaces at a molecular detail.[4] The Raman signal is enormously enhanced when the molecule is bonded to metallic clusters, mainly of silver or gold, of nanometer size. However, the changes between the intensities and wavenumbers of Raman and SERS spectra of a molecule are very often difficult to analyze because of their high sensitivity to the particular experimental conditions. This complexity is unavoidable given that metal-adsorbates interfaces are multicomponent systems involving macroscopic electrodes or nanometer-size metals clusters showing unknown local excess of charge at the SERS hot spot locations. The presence of the solvent and the electrolyte complicates even more the variables to be considered. When one compares the Raman and SERS spectra of a system it is usually observed changes of the relative intensities which implies different Raman selection rules.[4] May be this is the most controversial characteristic of SERS given that it is related to the involved

enhancement mechanisms.[5] Beside the intensities, the changes between Raman and SERS wavenumbers should be less controversial but very often also show a complex behavior. SERS spectra of cyanide anion has been studied in many papers, rendering almost impossible to summarize the reported results and the corresponding discussions which, in many cases, have led to opposite conclusions. The published works on the SERS of this molecule reveal the difficulty to account for the experimental behavior even in the case of a simple diatomic adsorbate. As an example, the discussion by Billman and Otto[6] of the SERS wavenumbers of the ν(CN) stretching band recorded on a silver electrode is a very enlightening example of the convoluted behavior of metal-molecule interfaces.

METHODS

DFT calculations of the properties of the closed shell stick-like complexes shown in Figure 1 have been carried out using the GAUSSIAN09 package[7] at several levels of theory in order to check the dependence of the results on the functional and the basis set. Raman spectra have been recorded with a resolution better than 2 cm^{-1} in a Renishaw InVia Qontor spectrometer working in macro conditions with a f:30 mm objective and using the 524.5 nm exciting line from an Ar^+ laser. A three-electrode cell controlled by a CH potentiostat model 600E and fitted with a pure silver working electrode, a platinum counter electrode and a saturated Ag/AgCl/KCl reference electrode has been used for spectroelectrochemical SERS experiments. Working electrode, previously polished with 0.3 and 0.05 μm alumina (Buehler) and immersed in an electrolyte solution of 0.1 M sodium sulfate or potassium chloride (Merck), is kept at a potential of -0.5 V and then electrochemically activated by means of seven 2 s pulses at +0.6 V in order to produce the required surface roughness for large SERS enhancement. SERS spectra have been recorded

from 0.01/0.1 M adsorbate/electrolyte aqueous solutions of potassium cyanide (Merck) and sulphate or chloride anions and using purified water from a Milli-Q system (resistivity over 18 MΩcm). Plotly-R program has been used for drawing the contour plots in Figure 7.[8]

RESULTS AND DISCUSSIONS

The silver-cyanide bond is formed mainly by charge donation from the 5-sigma orbital of CN^- to silver accompanied by back-donation. This 5-sigma orbital has antibonding character with respect to the intra-ligand C-N bond and, consequently, the stronger the M-A complex is, the stronger the C-N bond will be and higher vibrational wavenumbers are expected.[6-10] This is the reason why the wavenumbers of the ν(CN) stretching vibration in inorganic complexes[11] or in SERS are blue-shifted with respect to the Raman spectrum of cyanide in aqueous solution. Once the Ag-CN^- hybrid is formed, a continuous red-shift of the ν(CN) wavenumber should be expected as the electrode potential (E_V) becomes more negative because the excess of positive charge of the silver atoms decreases, implying a reduction of the charge injected by CN^- and, therefore, a weakening of the metal-adsorbate bond.

Figure 2 reproduces the collected data by Billman and Otto[6] of the dependence of the ν(CN) SERS wavenumbers on the electrode potential in the 2150-2090 cm^{-1} range when cyanide is adsorbed on silver using sodium sulphate as electrolyte. Three differentiated regions can be appreciated. This vibration is recorded at *ca*. 2140 cm^{-1} (region-C, Figure 2) or 2110 cm^{-1} (region-A) at more positive or negative potentials than -0.2 V_{SCE} (SCE, saturated calomel electrode), respectively. The first band is replaced by the second one with a sudden jump of 30 cm^{-1} occurring at this potential of -0.2 V_{SCE}. Furthermore, a dual behavior can be seen when E_V ranges from -0.2 to -1.5 V. The wavenumbers remain more or less constant at 2110 cm^{-1} from -

0.2 to -0.8 V (region-A) but show a linear dependence at potentials more negative than -0.8 V (region-B). Although the tuning of the wavenumbers by an applied electric field is a very known effect (vibrational Stark tuning or shift)[12,13] the surprising result is that region-A is almost

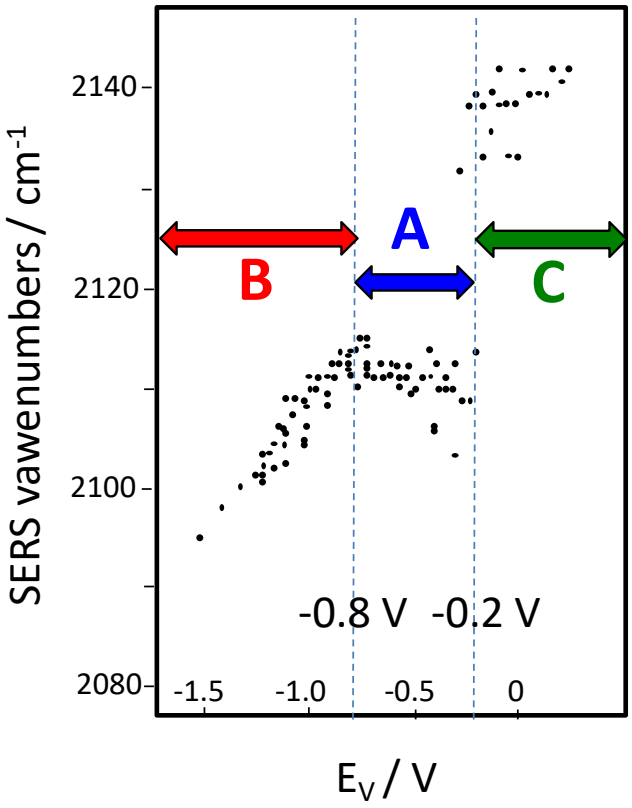

Figure 2. Data collected by Billman and Otto (ref. 6) of the dependence of the SERS wavenumbers of the ν(CN) stretching vibration on the electrode potential (E_V *vs*. SCE and using sulphate as electrolyte).

insensitive to the potential and only region-B (from -0.8 to -1.5 V) shows the expected linear dependence with positive slope. Previously published DFT calculations including external electric fields predict an almost constant Stark tuning rate (cm^{-1}/V) of the ν(CN) band in the

entire range (positive and negative) of applied fields[14] and, therefore, no jumps or changes in the rate should be registered in agreement with the expected behavior for a Stark effect.[15] These SERS spectra of silver-cyanide characterized by differentiated regions when sulphate salts are used as electrolyte are reproducible and has been reported by others authors as, for instance, by Benner et al.[16] who also have detected it on copper.[17]

Two hypothesis are usually invoked in order to explain the behavior of the vibrational wavenumbers of adsorbed cyanide: The presence of $[Ag^{+}\text{-}(CN^{-})_x]^{1-x}$ surface complexes with different coordination numbers or the adsorption of a single cyanide ion on nonequivalent local sites of the metallic surface.

The cyanide-Ag system has been repeatedly analyzed by correlating the dependence of the $\nu(CN^{-})$ SERS wavenumbers on the electrode potential with those of free/solvated ligand and different $Ag^{+}\text{-}(CN^{-})_n$ complexes which would follow the trend:[6,16,18,19]

$$\Leftarrow E_{V\text{-}} \quad \nu(CN^{-}) < \nu(Ag\text{-}(CN)_4^{3-}) < \nu(Ag\text{-}(CN)_3^{2-}) < \nu(Ag\text{-}(CN)_2^{-}) < \nu(Ag\text{-}CN) \quad E_{V+} \Rightarrow$$

$$\Leftarrow E_{V\text{-}} \quad 2080\ cm^{-1} < 2097\ cm^{-1} < 2105\ cm^{-1} < 2135\ cm^{-1} < 2164\ cm^{-1} \quad E_{V+} \Rightarrow$$

According to this correlation, negative ($E_{V\text{-}}$) potentials should be related to species located on the left of this series given that a red-shift of the SERS wavenumbers is observed in these conditions. The published discussions about this correlation are very confusing. For instance, the 2110 and 2140 cm^{-1} bands have been assigned to $Ag\text{-}(CN)_3^{2-}$ and $Ag\text{-}(CN)_2^{-}$ surface complexes, respectively,[16,18] which could explain the jump of 30 cm^{-1} between regions-C and -A, but Billmann and Otto[6] propose an alternative assignment. Although a single silver adatom of the surface could accommodate more than one CN^{-} it is not easy to understand how the number of

negatively charged ligands bonded to a silver atom increases as the electrode potential is more negative, when a stronger repulsion between the negative charge of the electrode and the anionic ligand is expected. Negative potentials diminish the positive charge of the metallic atoms and therefore, there should be a lower affinity of cyanides for the surface. Finally, the major objection concerns the bimodal behavior of regions-A and B given that the existence of different $[Ag^{+}\text{-}(CN^{-})_x]^{1-x}$ complexes do not explain why the wavenumber of one of them remain constant (region-A) while the another one is sensitive to the electrode potential (region-B).

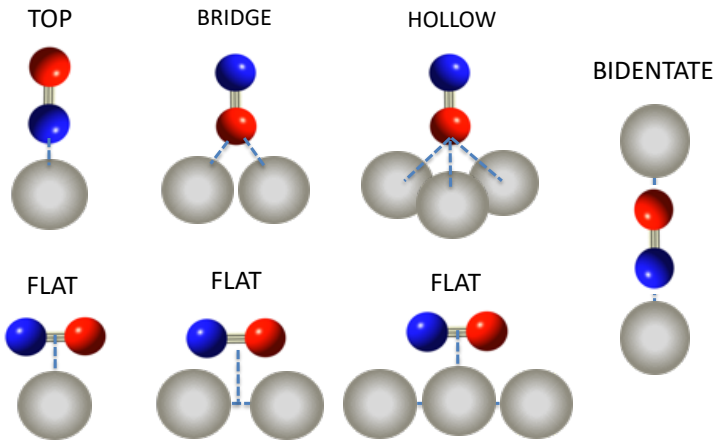

Figure 3. Models of cyanide adsorbed on different local sites of metal surfaces.

The discussion becomes even more uncertain if the unavoidable presence of nonequivalent atomic sites on a heterogeneous surface is considered.[10] In addition to the existence of Ag-CN complexes with several stoichiometries, different sites of adsorption or surface reorientation (or tilting) of the molecule[10,20] are very often invoked in order to explain the changes induced by the adsorption or by the applied potential. Figure 3 shows different coordination models proposed for a single CN^{-} adsorbed on different local sites which are usually classified as top, flat, bridge and hollow, respectively.[10,14] Except in the flat case, cyanide can be bonded through the nitrogen

or the carbon atoms, although it is generally assumed that the silver complexes through the carbon (complex-C, Ag-CN) are more stable than the corresponding complex-N (Ag-NC).[3,21]

Table 1 summarizes the B3LYP[22,23]/LanL2DZ[24,25] calculated energies of formation ($\Delta E_f=E_{MA}-(E_M+E_A)$) of different M-A systems where cyanide is bonded to models of Figure 3. The set of results point to a simple conclusion: Top coordination is the most stable complex in each case and the bonding through the carbon is the preferred option irrespective of the density of charge of the silver clusters (q_{eff}). Therefore, theoretical calculations predict that complex-C on top of a single silver atom (top-C) should be the most stable coordination at any surface excess of charge, i.e., at any electrode potential. B3LYP functional has been selected due to its good estimations of energies and vibrational wavenumbers[26] and it can be seen in the same Table that both quantities correlate well for each type of complexes in such a way that stronger complexes have higher wavenumbers.

The dependence of the B3LYP/LanL2DZ energies of formation on the effective charge q_{eff} of the stick-like systems (Figure 1) with top-N and top-C coordination is shown in Figure 4a. Top-C complexes are somewhat more stable than the corresponding N-bonded ones in the entire range of effective charges $q_{eff}=\pm0.33$ a.u., but both series of data show two different trends depending on the sign of q_{eff}. For instance, top-C complexes are very stable at positive densities of charge due to the attractive Coulombic interaction between the opposite charges of both moieties with energies of -6.59 and -5.39 eV (-153 and -125 Kcal/mol) for $q_{eff}=+0.33$ and +0.08 a.u., respectively. The repulsive complexes with $q_{eff}<0$ are much less stable and their energies range from 0.98 to -1.90 eV (+23 and -44 Kcal/mol) for the respective $q_{eff}=-0.33$ and -0.08 a.u. values. Therefore, the tuning amplitude of the energies of formation is three times larger in the

Table 1. B3LPY/LanL2DZ calculated energies of formation ΔE_f and vibrational wavenumbers of the $\nu(CN^-)$ stretching mode for different models of coordination shown in Figure 3.

Effective Charge q_{eff} (a.u.)	Ag_n^q cluster	Type of Complex	ΔE_f Energy (eV)	Wavenumber (cm^{-1})
+1	Ag^+	top-C	-7.83	2165.7
		top-N	-7.31	2048.6
		flat	-7.03	1931.9
+0.33	Ag_3^+	top-C	-6.65	2157.7
		top-N	-6.21	2048.4
		hollow-C	-4.74	2042.8
		hollow-N	-4.94	1954.9
		flat	-4.89	1994.0
0	Ag_2^0	top-C	-2.46	2120.5
		top-N	-2.17	2052.0
		bridge-C	-0.72	2037.5
		bridge-N	-0.78	2001.2
		flat	-0.77	2012.0
-0.33	Ag_3^-	top-C	0.98	2082.6
		top-N	1.14	2042.0
		hollow-C	2.41	2012.2
		hollow-N	2.44	2000.4
		flat	dissociates	
+1/+0.33	Ag^+/Ag_3^+	Ag^+-NC^--Ag_3^+	-9.85	2190.8
		Ag^+-CN^--Ag_3^+	-9.74	2205.6
+1/+1	Ag^+/Ag^+	Ag^+-CN^--Ag^+	-10.53	2208.8
		Isolated CN^-		1995.2

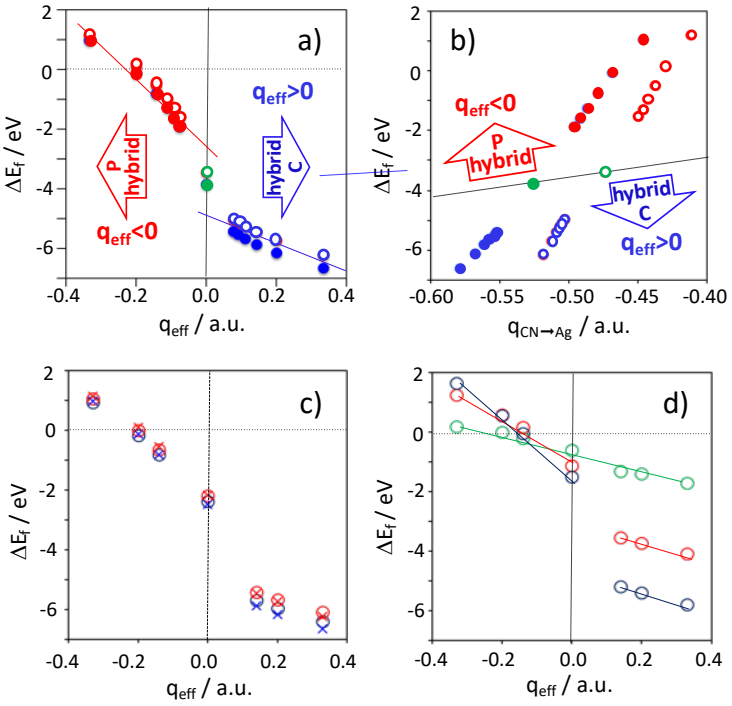

Figure 4. Dependence of the B3LPY/LanL2DZ calculated energies of formation (ΔE_f) of top-C (full circles) and top-N (empty circles) systems on a) the effective charge (q_{eff}) of the stick-like complexes shown in Figure 1 and b) on the Mulliken charges injected from cyanide to the silver clusters ($q_{CN\rightarrow Ag}$). Comparison between the dependence on q_{eff} of c) the B3LPY/lanL2DZ (crosses) and M06-HF/lanL2DZ (circles) energies of the top-C (blue) and top-N (red) $[Ag_n^{q}\text{-}CN]^{q-1}$ linear systems and d) the M06-HF/lanL2DZ energies of the corresponding complexes of neutral pyridine (green) and the isonicotinate anion bonded through the nitrogen (red) or the carboxylate (blue).

repulsive case ($q_{eff}<0$) than in the attractive one ($q_{eff}>0$), which is reflected in the corresponding slopes. This means that the electronic structure of the surface complex is much more polarizable at potentials more negative than the potential of zero charge of the electrode ($E_{V,PZC}$) having metastable structures with positive ΔE_f values at very negative densities of charge (+0.98 eV,

q_{eff}=-0.33 a.u.) where the system is preserved against dissociation due to the existence of a local minimum.[1] The energies of the complexes with q_{eff}>0 (ca. -140 Kcal/mol) remain almost constant and are in the order of a chemical bond. Therefore, these complexes can be considered as chemisorbed species (C-hybrid) which are strongly bonded due to the attractive interaction between the positive charge of the electrode and the negative charge of the adsorbate. On the contrary, the metal-molecule bond is significantly weaker at q_{eff}<0 as expected for a physisorbed complex (P-hybrid) and scans a large range of energies (ΔE_f=67 Kcal/mol, from q_{eff}=-0.33 to -0.08 a.u.). Chemisorbed and physisorbed electronic structures are separated by the Ag_{20}^{0}-CN^- neutral complex (q_{eff}=0 a.u.) whose energy amounts to -3.81 eV (-88.6 Kcal/mol), a similar value to the average of the respective energies of the least charged $Ag_{13}^{q=\pm1}$-CN^- complexes (-3.64 eV/-84.5 Kcal/mol, q_{eff}=±0.08 a.u.). Therefore, it is expected a more or less smooth transition between physisorbed and chemisorbed structures around the potential of zero charge of the electrode which connect both branches.

In accordance with many previously published discussions on metal-cyanide complexes[3,6] B3LYP results predict a donation of negative charge from cyanide to silver clusters $q_{CN\rightarrow Ag}$ when the surface complex is formed, even at very negative densities of charge of the physisorbed species. The calculated Mulliken charges injected into the metallic clusters range from -0.4 to -0.6 a.u. These are significant values and consequently, the ground electronic state of these systems can be considered as true molecule-to-metal charge transfer states in all the q_{eff} range, i.e., at any electrode potential. Both, the large values of ΔE_f and $q_{CN\rightarrow Ag}$ are related to the strong affinity of cyanide to be specifically adsorbed on silver electrodes. In this respect, the energies of the respective linear complexes correlate very well with the donated charge from the cyanide to the silver clusters. Figure 4b shows the linear dependence found between both quantities at any

q_{eff} but a differentiated behavior can be appreciated for C- and P-hybrids once again. The respective points are twice more compressed at positive than at negative densities of charge indicating that the P-hybrid is more polarizable by the applied potential while the electronic structure of the chemisorbed species remains very robust and almost unchanged. Complexes bonded through the carbon or the nitrogen atoms have analogous behaviors although the injected charges $q_{CN\rightarrow Ag}$ for the less stable complex-N are ca. 20% smaller in spite of having very similar energies of formation.

The respective ΔE_f energies of the cyanide-silver complexes have been recalculated at the M06-HF[25]/LanL2DZ level (Figures 4c and 4d) in order to be compared with the previously reported results for isonicotinate anion (In^-)[1] and neutral pyridine.[2] Isonicotinate bonded to silver through either the carboxylate (OIn^-) or the pyridinic nitrogen (Nin^-) shows also the bimodal behavior for physisorbed and chemisorbed complexes, while in the case of a neutral adsorbates like pyridine the effect of the sign of the density of charged of the metal is very weak and the differences are so small that a smooth linear trend of ΔE_f at any q_{eff} can be assumed.[1,2] Both, OIn^- and Nin^- show similar behaviors in the repulsive region with $q_{eff}<0$ a.u. but OIn^- becomes clearly more stable when the silver cluster is positively charged. The cyanide-silver complex is even more stable than the preferred case of isonicotinate bonded to silver through the carboxylate group.

Theoretical results do not depend significantly on the size of the basis set as can be seen in in Figure S1a, where B3LYP/lanL2DZ and B3LYP/Def2-TZVPP[28] calculated ΔE_f are compared. Slightly less stable energies are calculated with the larger basis but the injected charges show some differences (Figure S1b). Def2-TZVPP gives larger amount of transferred charge, what

means that the ground electronic state should have even more CT character. The behaviors are quite similar for the two bases in the case of the strong C-hybrid, but the B3LYP/Def2-TZVPP values of $q_{CN \rightarrow Ag}$ for the physisorbed species show a minor slope and therefore, range a more spread interval of injected charges.

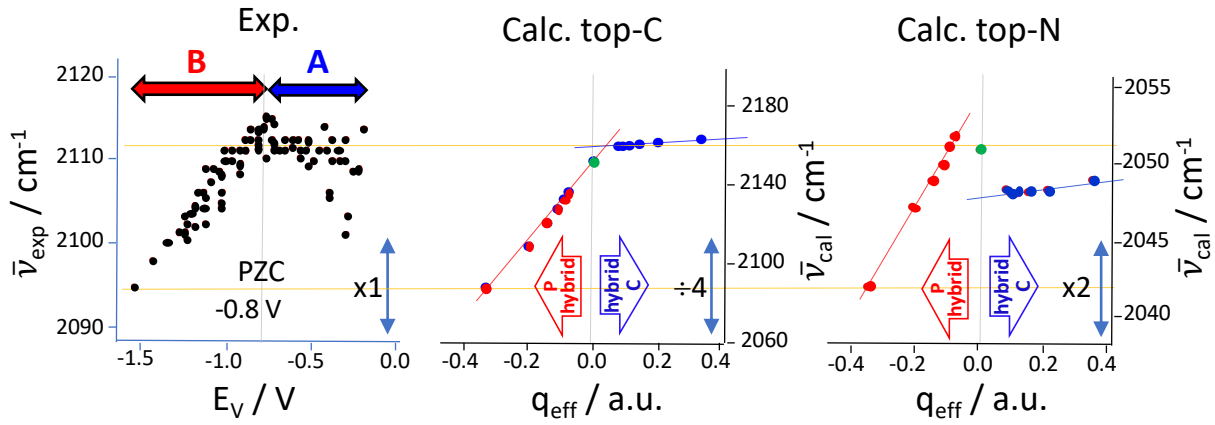

Figure 5. Effect of the electrode potential on the experimental SERS wavenumbers of the ν(CN^-) stretching vibration collected by Bilmann and Otto[6] and dependence of the B3LPY/LanL2DZ calculated wavenumbers on q_{eff} of top-C and top-N linear $[Ag_n^q\text{-}CN]^{q-1}$ complexes.

Summarizing, calculated properties such as bond strengths, injected charges and energies of the charge transfer states[1] point to the existence of two electronic structures of different nature of a particular metal-molecule hybrid but this conclusion has not yet been experimentally supported. Figure 5 shows the experimental wavenumbers of the ν(CN) mode collected by Billman and Otto[6] and the respective B3LYP/LanL2DZ calculated values for the two sets of top-C and -N complexes. The correlation between the values of the experimental electrode potentials and the theoretical q_{eff} parameter has been previously discussed.[29] The huge energy gain[30,31] when

the electrode potential tunes the energies of the CT states[32] and the selective enhancement of mode 9a at very negative potentials in the SERS of pyridine[33] allow to relate the full range of potentials covering all the regions (0 to -1.5 V) to the full range of charge densities of the clusters (q_{eff}=±0.33 a.u.). Under these conditions, the potential of zero charge of the electrode (ca. -0.8 V),[34] which coincides with the turning point between de potential dependent region-A and the constant region-B, can be properly related to the neutral complex [Ag_{20}^{0}-CN^{-}] with q_{eff}=0 a.u. It is evident from Figure 5 the qualitative agreement between experimental and the calculated results. As can be seen, top-C and -N set of data predict the same trend: A constant wavenumbers at positive densities of charges and a continuous and linear red-shift at negative q_{eff}. The electrode potential or the charge densities of the silver clusters are unable to modify significantly the ν(CN) wavenumbers at positive excesses of charge. The very strong structure of the C-hybrid prevents the weakening or the strengthening of the CN bond in both, the top-C and -N cases, in such a way that this property is even less potential dependent that the corresponding bond energies. The polarizable physisorbed species show in turn the expected behavior for the classical vibrational Stark effect and the respective wavenumbers are linearly red-shifted as q_{eff} is made more negative.

Although top-C and -N have similar trends the respective amplitudes of the wavenumber shifts ($\Delta\bar{\nu} = \bar{\nu}_{qeff=0} - \bar{\nu}_{qeff=-0.33}$) are quite different at negative q_{eff}. $\Delta\bar{\nu}$ of 64 and 8 cm^{-1} are calculated for the P-hybrid of top-C and top-N systems, respectively, while an experimental value of ca. 17 cm^{-1} is derived from region-B, which gives an experimental Stark tuning rate of $\Delta\bar{\nu}_{exp,V}$=24 cm^{-1}/V. If the relationship between the potential and the effective charge (1.5 V ∽ 0.66 a.u.) is assumed, this value can be compared with the calculated rates for top-C and -N systems at q_{eff}<0 a.u.

which amount to $\Delta\bar{\nu}_{cal,qeff}$= 85 and 11 cm^{-1}/V, respectively. Although the calculated energies of the complexes bonded through the carbon or the nitrogen are very similar, no evidences of the simultaneous observation of SERS signals from both perpendicular orientations of cyanide are detected. In such case two separated series of bands shifted tens of cm^{-1} would be recorded in the entire range of potentials given that the calculated wavenumbers for the neutral complex-C and -N are 2145 and 2050 cm^{-1}, respectively. In a recent work on the electrochemical SERS wavenumbers of pyridine[29] we have estimated that the relationship between the experimental and B3LYP/LanL2DZ calculated Stark tuning rates is $\Delta\bar{\nu}_{exp,V} = \Delta\bar{\nu}_{cal,qeff}/3.5$, a value in good agreement with the overestimated values calculated for complex-C. This result, as well as the large jump between the wavenumbers of the C- and the P-hybrid around q_{eff}=0 a.u. in the case of the top-N complex, allows to discard the coordination through the nitrogen atom as the species responsible for the SERS spectra. Very similar results are obtained at B3LYP/Def2-TZVPP, wB97-XD[35]/lanL2DZ or M06-HF/lanL2DZ levels of theory (Figures S2 and S3).

Finally, region-C cannot be explained on the basis to the set of linear complexes shown in Figure 1. Regions-A and -C are not dependent on the electrode potential, being characterized by unshifted wavenumbers of 2110 and 2140 cm^{-1}, respectively. This sudden jump of 30 cm^{-1} has been reported by several authors[6,16] and is also observed in our SERS records using sulphate as electrolyte (Figure 6a) but cannot be reproduced by the theoretical calculations even by considering systems with more positive q_{eff} values than +0.33 a.u. For instance, The B3LYP/lanL2DZ calculated wavenumber for the Ag^+-CN^- complex is 2166 cm^{-1} (Table 1), only 8 cm^{-1} blue-shifted with respect to the value for Ag_3^+-CN^- (2158 cm^{-1}, q_{eff}=+0.33 a.u.). This Ag^+-CN^- complex has the largest q_{eff}=+1 a.u. and would corresponds to cyanide bonded to a fully oxidized and isolated silver cation that should no longer be part of the metal electrode or

nanoparticle. Billman and Otto[6] report the formation of a surface film at positive electrode potentials related to an anodic peak at +0.2 V_{SCE} in the voltammogram. These authors suggest that this surface film would consist of an unknown number of monolayers of Ag-CN originated by the incorporation of cyanide to the structure of the solid electrode. The peak at +0.2 V_{SCE} could be due to the oxidation of silver atoms located at particular positions of the surface with oxidation potentials more negative than the required one for the massive dissolution of the electrode. This would mean that some silver cations leave the electrode around this potential and can be trapped by solvated or adsorbed cyanide. We propose that the band of region-C is from surface complexes where cyanide acts as a bidentate ligand bonded to two silver atoms (Figure 3). Bidentate complexes Ag^{+}-NC^{-}-Ag_3^{+}, Ag^{+}-CN^{-}-Ag_3^{+} and Ag^{+}-CN^{-}-Ag^{+} are the simplest approaches to the surface film proposed by Billman and Otto[6] and could explain the wavenumber jump given that the calculated wavenumbers amount to 2191, 2206 and 2209 cm^{-1}, respectively.

In order to confirm this hypothesis new SERS experiments have been carried out by using chloride instead of sulphate as electrolyte. The spectra look like similar in both cases but the main difference is that region-C is missing when chloride anions are used (Figure 6). Chloride have much more affinity than sulphate to bond to silver cations and can compete against cyanide in favorable conditions given the much higher concentration of electrolyte than of adsorbate. The different solubility of the respective silver salts can control the formation of bidentate cyanide complexes and, therefore, the presence of the characteristic band of region-C at 2140 cm-1, being expected its disappearance using fluoride and the reappearance when bromide is used.

The contour diagrams corresponding to the SERS recorded with potassium sulphate and chloride as electrolytes are drawn in Figure 7 where it can be seen the existence of three different regions in the case of sulphate, the disappearance of region-C when chloride is used, the constant wavenumbers shown by regions-A and -C and the red-shifts of the ν(CN) SERS wavenumbers in region-B.

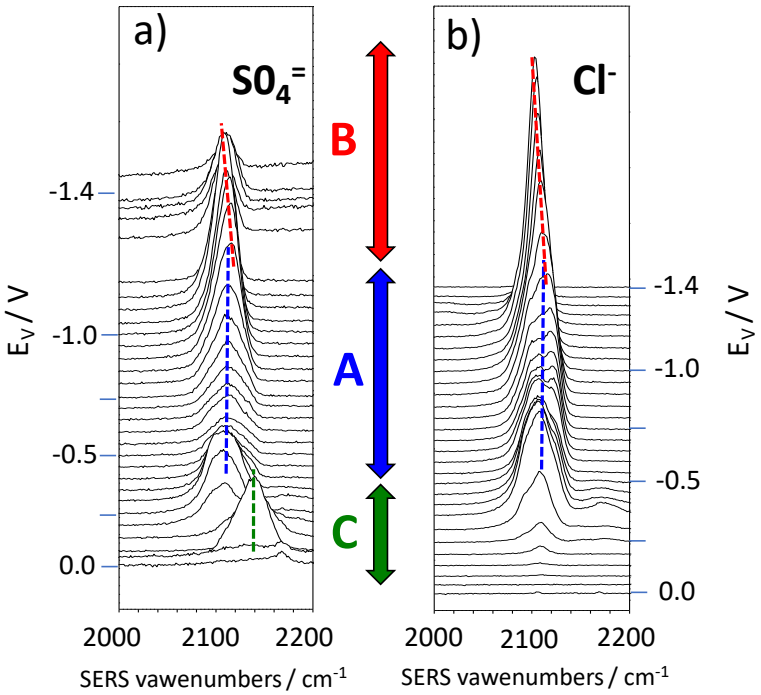

Figure 6. Dependence of the ν(CN) SERS band on the electrode potential using a) sodium sulphate or b) potassium chloride as electrolyte (E_V *vs*. Ag/AgCl/KCl sat.).

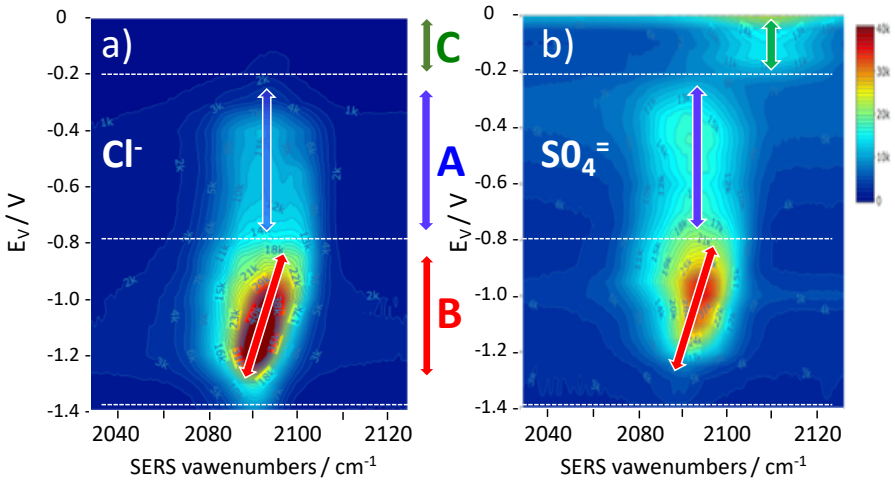

Figure 7. Contour plots of the effect of the electrode potential on the SERS spectra shown in Figure 6 using a) potassium chloride or b) sodium sulphate as electrolyte (E_V vs. Ag/AgCl/KCl sat.).

CONCLUSIONS

The behavior of the SERS of cyanide adsorbed on a silver electrode has been discussed, for the first time, on the basis of a dual electronic structure of the metal-molecule hybrid. These structures are selected by the sign of the charge of the metal and have the same rough geometry but differentiated physicochemical properties. Cyanide forms a very strong chemisorbed complex (C-hybrid) under positive excess of charge of the surface in such a way than its electronic structure remains almost unaffected by the applied potential. On the contrary, a weaker a very polarizable physisorbed species (P-hybrid) is formed at potentials more negative than that of the zero charge of the electrode. Vibrational wavenumbers of the ν(CN) stretching mode are very sensitive to these two kinds of electronic structures showing constant values when the C-hybrid is formed and the expected vibrational Stark tuning in the case of the polarizable P-

hybrid. Theoretical calculations on the properties of cyanide bonded through the carbon to a single silver atom with different excesses of charge are able to account for this differentiated behavior. Moreover, it is predicted than the two electronic structures of the complex also should show different trends for both the bond energies and the injected charges in the electrode with similar characteristics than those of the respective wavenumbers.

Spectroelectrochemical experiments of a very simple diatomic molecule like cyanide is a good example of the difficulty of analyzing SERS spectra. This is due to the inherent complexity of the metal-molecule interfaces where the subtle chemical interaction between single molecules bonded to large systems, as massive electrodes or nanoparticles, are modulated by external electric potentials. These interfaces are involved in many others important processes taking place in electrochemistry, heterogeneous adsorption or catalysis, or in technological devices for energy conversion or in the electronic transport through molecular junctions which is the basis of molecular electronics. Experiments in these fields very often show a sharp dual behavior which is usually explained on the basis of not always well supported assumptions such as the reorientation of the adsorbate, the existence of two or more surface complexes with different stoichiometries, or the adsorption on different local sites of the metallic surface. This kind of standard analysis have, obviously, some chemical basis but do not help to improve the understanding of the complex structure and capabilities of these systems. In the case of the SERS of cyanide these hypotheses cannot explain why the vibrational wavenumbers of a particular orientation, surface complex or local site are very dependent on the electrode potential and why another one is unsensitive to this parameter. Sometimes these results have been blamed to other origins. For instance, in the paper by Dornhaus et al.[36] on the SERS of several adsorbates including cyanide one can read: “Extending the voltage to values more negative than the

potential of zero charge (PZC), caused shifts in peak positions to become more pronounced. It has been suspected[37] that these small shifts of 2-3 cm^{-1} in the range between 0 to -0.6 V might be instrumental artifacts associated with the mechanical movement of the gratings in a conventional spectrometer".

Finally, the existence of two different electronic structures for a particular metal-molecule system have consequences not only on properties of the ground state like the here discussed but on the overall electronic building of the surface complex, particularly on the nature and the dependence of the energies of the excited metal-molecule charge transfer states on the electrode potential.[1] This is an important result which can open new capabilities for improving devices where electronic transport through metal-molecule interfaces takes place. If the close relationship between the electronic structure of metal-molecule interfaces and the SERS spectra[36] is confirmed in future works SERS could became a very powerful tool to get insight into the structure and properties of interfaces at a molecular level.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:.

Figures showing calculated results of bond energies, injected charges and vibrational wavenumbers at different levels of theory

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