

## SERS and DFT Study on 4-Methylpyridine Adsorbed on Silver Colloids and Electrodes

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Surface-enhanced Raman scattering (SERS) spectra of 4-methylpyridine are obtained in silver hydrosol and compared with those obtained in an electrochemical cell. The use of density functional theory (DFT) calculations allows one to interpret the SERS data and collect information on the structures of the complexes formed on the metal surface as well as on the Raman enhancement mechanism.

## Introduction

The surface-enhanced Raman scattering (SERS) effect was first observed on silver electrodes,<sup>1</sup> roughened by oxidation–reduction cycles (ORC), but successively different SERS-active substrates, mainly metal colloidal suspensions, have been employed.<sup>2</sup> The advantages of the latter with respect to the electrodes in an electrochemical cell are due to the large adsorption capability and the simplicity in the preparation of the SERS-active substrate. Moreover, the adsorption of ligands can be monitored by observing in the UV–visible absorption spectrum the plasmon resonance bands due to the excitation of the conduction electrons localized at the metal colloidal surface. Finally, the presence of metal nanoparticles dispersed in a dielectric continuum closely corresponds to the interpretation of the Raman enhancement effect based on the electromagnetic model. Otherwise, the metal colloids undergo instability, due to aging or addition of ligands and spectral interference of species deriving from the preparation method. This affects the adsorption process and, consequently, the enhancement mechanism; thus, it is not trivial that the same spectral evidence can be detected on different substrates. However, a close correspondence was found between the SERS spectra of diazines in silver hydrosol and those detected in an electrochemical cell.<sup>3</sup> Varying the electrode potential affects the charge transfer between metal and molecule and provokes changes in the SERS intensities of the adsorbate or the adsorption of different species, as in the case of 2-amino-5-nitropyridine, which was adsorbed as an anion at potentials more positive than  $E = -0.5$  V (SCE).<sup>4</sup> In that case, the spectral data resulted closely comparable with those obtained in silver hydrosol by varying the pH of the aqueous medium.

Recently, the potential dependence of the SERS intensities of 4-methylpyridine adsorbed on silver electrodes has been studied by considering a charge-transfer mechanism.<sup>5</sup> In the present work, the adsorption of the same ligand is investigated in silver hydrosol by varying the pH in order to correlate the SERS frequencies and intensities to those detected on silver electrodes at different potentials. Moreover, the employment of density functional theory (DFT) calculations, performed on molecule/metal interaction models, allows one to interpret the SERS data and collect information on the structure of surface

complexes as well as on the Raman enhancement mechanism. This computational approach allowed us to identify the adsorbed species for different ligands and to reproduce satisfactorily SERS frequencies and relative intensities.<sup>6,7</sup>

## Experimental Section

4-Methylpyridine (Merck, purity >98%), twice purified by distillation, was added ( $10^{-3}$  M concentration) to silver hydrosols, prepared according to Creighton's procedure,<sup>2</sup> aged a week to prevent the formation of reduction products.<sup>8</sup> The pH value of the colloidal dispersions ( $\sim 9$ ) was adjusted by the addition of NaOH or HClO<sub>4</sub>. NaCl ( $10^{-3}$  M) was added to the silver hydrosols to increase the SERS intensities of the ligand.

Raman measurements were performed by using a Jobin-Yvon HG-2S monochromator, a cooled RCA-C31034A photomultiplier, and the 514.5 nm exciting line supplied by an Ar<sup>+</sup> laser, with a power of 50 mW and a  $4\text{ cm}^{-1}$  resolution. Power density measurements were performed with a power meter instrument (model 362; Scientech, Boulder, CO), giving an accuracy of  $\sim 5\%$  in the 300–1000 nm spectral range. The same laser line was employed by Arenas et al.<sup>5</sup> for the experiments at silver electrodes.

The SERS intensities observed in silver hydrosols were relative to the intensity of the strong SERS band around  $1600\text{ cm}^{-1}$ , which was chosen as the internal standard, closely following what was performed by Arenas et al.<sup>5</sup> The addition of NaCl to the silver colloidal suspension ensured the possibility of comparing the SERS experiments at different pH values with those previously performed in an electrochemical cell at different electrode potentials with a 1 M KCl aqueous solution as the electrolyte and a saturated Ag/AgCl/KCl reference electrode.<sup>5</sup>

## Calculation Method

All density functional theory (DFT) calculations were performed with the Gaussian 98 package<sup>9</sup> using the combination of the B3LYP exchange correlation functional along with the Lanl2DZ basis set. The structures of 4-methylpyridine and its surface complexes with Ag<sup>+</sup> and Ag<sup>0</sup> were optimized with a *tight* criterion, and the harmonic frequencies were calculated by using an improved grid to compute the integrals (Integral-Grid = 199 974). A uniform scaling factor of 0.9833 has been adopted for all the computed frequencies corresponding to the vibrational normal modes, as recently done in the case of pyrazole adsorbed on silver.<sup>6</sup>

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**TABLE 1: SERS Frequencies ( $\text{cm}^{-1}$ ) and Intensities of 4-Methylpyridine Adsorbed on Silver Colloids and Electrodes**

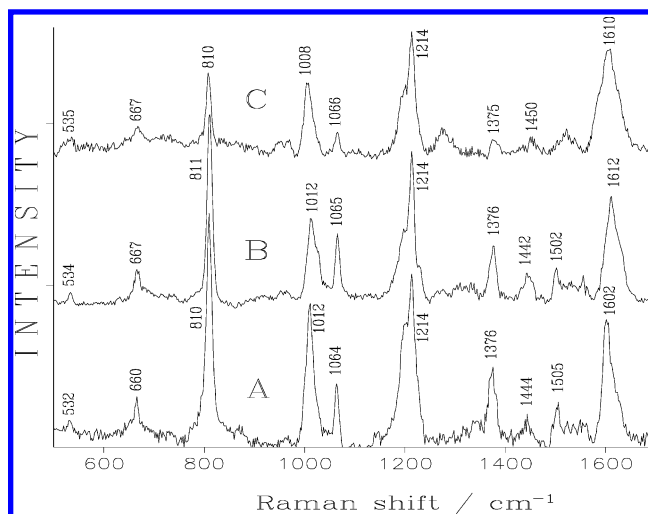
Silver Colloid <sup>a</sup>							
pH 6		pH 8.5		pH 11			
freq	int	freq	int	freq	int		
1602	100	1612	100	1610	100		
1376	51	1376	44	1375	20		
1214	138	1214	144	1214	117		
1067	56	1065	55	1066	24		
1012	116	1012	70	1008	74		
810	186	811	171	810	68		
532	3	534	10	535	20		
Silver Electrode <sup>b</sup>							
$E = 0.00 \text{ V}$		$E = -0.25 \text{ V}$		$E = -0.50 \text{ V}$		$E = -0.75 \text{ V}$	
freq	int	freq	int	freq	int	freq	int
1606	100	1612	100	1614	100	1612	100
1380	110	1380	91	1380	42	1376	31
1216	195	1213	293	1213	104	1213	103
1067	100	1065	122	1065	49	1065	35
1013	145	1013	217	1015	145	1013	141
812	264	812	228	810	100	808	86
		537	41	535	41	533	62

<sup>a</sup> Present measurements. <sup>b</sup> Reference 5.

## SERS Results

As generally accepted, there are two main contributions to the surface Raman enhancement.<sup>10–12</sup> The electromagnetic mechanism, related to the excitation of the surface electrons of the metal, is able to produce an enhancement of the Raman signal by as much as 6 orders of magnitude. The chemical effect, which arises when the ligand is adsorbed on the metal, forming chemical bonds with the active sites (adatoms) of the surface, gives enhancement factors much smaller, at most  $10^2$ .<sup>13,14</sup> Nevertheless, this contribution cannot usually be considered as negligible, since it strongly affects the relative intensities of the SERS bands, depending on both the strength and direction of the molecule–metal bonds. The latter modify the electron distribution in the molecule, changing the force constants, mainly those involving the atoms closer to the substrate. Hence, the chemical interaction is responsible for the frequency shifts in the vibrational spectra, but larger changes are expected for the vibrational intensities, since chemisorption strongly affects the derivatives of the polarizability and of the dipole moment with respect to the normal coordinates of the ligand, involving also atoms far from the metal substrate.

In the case of 4-methylpyridine (hereafter, 4MePy) adsorbed on silver electrodes, no relevant frequency shifts occurred by varying the electrode potential, while more significant variations were observed in the SERS intensities (Table 1). By referring to the intensity of the band at  $\sim 1600 \text{ cm}^{-1}$ , most bands decreased as the potential became more negative, except for the band at  $\sim 1013 \text{ cm}^{-1}$ , whose intensity remained almost constant, and for that at  $\sim 535 \text{ cm}^{-1}$ , which, instead, increased in intensity. Figure 1 reports the SERS spectra of 4MePy in silver hydrosol, at different pH values by adding NaOH or  $\text{HClO}_4$ , while in Table 1 the intensities of the prominent bands are compared with those detected on silver electrodes by adopting in both cases the SERS band around  $1600 \text{ cm}^{-1}$  as the internal standard. Below  $400 \text{ cm}^{-1}$ , no intense SERS band is observed in the silver hydrosol, as well as in the electrochemical cell. The Ag–N stretching band, which usually occurs in the low-frequency region ( $200\text{--}250 \text{ cm}^{-1}$ ), is masked by the overlapping of the Ag–Cl stretching band for SERS experiments



**Figure 1.** SERS spectra of 4-methylpyridine ( $10^{-3} \text{ M}$ ) in silver hydrosol: pH 6 (A); pH 8.5 (B); pH 11 (C). NaCl concentration,  $10^{-3} \text{ M}$ ; exciting line, 514.5 nm.

in an electrochemical cell with KCl as the electrolyte as well as in colloidal suspension with the addition of NaCl. The presence of chloride anions in the aqueous suspension ensures experimental conditions similar to those in the electrochemical cell with KCl as the electrolyte. A comparison with the SERS intensities detected on an electrode at  $E \leq -1.0 \text{ V}$  (SCE) cannot be proposed because of possible ligand reactions at very negative potentials. By inspection of Table 1, it is possible to observe that the SERS bands of 4MePy in silver hydrosol are coincident with those detected on silver electrodes. Moreover, by increasing the pH of the silver hydrosol, the bands generally decrease in intensity, mainly that occurring around  $810 \text{ cm}^{-1}$ , as well as in the electrochemical cell by shifting the electrode potential to more negative values. Actually, in silver colloids, hydroxide ions are usually coadsorbed onto the metal particles, making the metal surface negatively charged. In other words, in the absence of an applied potential such as in an electrochemical cell, the surface charge of the silver particles is controlled by the adsorption of hydroxide ions. In an acidic medium, instead, these ions are removed from the surface, ensuring a more efficient charge transfer from the nitrogen lone pair of the ligand to the metal. This, according to a photoassisted enhancement mechanism,<sup>15</sup> induces an intensity increase, mainly for the vibrations occurring along the charge-transfer direction. In Table 2, the Raman bands of 4MePy are compared with the SERS ones and assigned according to DFT calculations. The SERS band observed at  $\sim 810 \text{ cm}^{-1}$ , which reaches the maximum intensity at an acidic pH in silver hydrosol and at  $E = 0 \text{ V}$  (SCE) in an electrochemical cell, corresponds to a vibration occurring along the charge-transfer direction, exhibiting large carbon–methyl stretching contribution.

## DFT Calculations

To predict and to interpret the SERS spectra of an adsorbate, it would be useful to have a computational tool able to reproduce with good accuracy not only the frequencies but also the relative intensities. Different computational approaches have been recently proposed. The intensities of the SERS bands that at negative electrode potentials showed the highest enhancements have been interpreted on the basis of the calculated Raman intensities of the negatively charged molecule. This method was applied successfully by Arenas and co-workers to the SERS spectra of heteroaromatic compounds.<sup>5,16–20</sup> Corni and Tomasi,<sup>21</sup>

**TABLE 2: Observed and Calculated Frequencies (below 1700 cm<sup>-1</sup>) of 4-Methylpyridine<sup>a</sup>**

species	IR liquid <sup>b</sup>	Raman liquid	SERS		calcd			assignment
			A	B	C	D	E	
A'' (A <sub>2</sub> )					15	24	16	methyl torsion
A'						71	39	Ag-N wagging
A''						128	70	Ag-N-C bending
A'						192	93	Ag-N stretching
A' (B <sub>1</sub> )		215			208	233	216	methyl rocking
A'' (B <sub>2</sub> )		345			335	345	339	C-C-Me bending
A'' (A <sub>2</sub> )					388	399	387	ring torsion
A' (B <sub>1</sub> )	485	485	486	486	497	500	498	ring torsion
A' (A <sub>1</sub> )	522	514	532	535	514	548	524	ip ring deformation
A'' (B <sub>2</sub> )		670	660	668	673	667	671	ip ring deformation
A' (B <sub>1</sub> )	728				748	732	742	ring torsion
A' (A <sub>1</sub> )	801	802	810	808	793	808	797	C-Me stretching + ip ring deformation
A' (B <sub>1</sub> )					822	831	825	C-H wagging
A'' (A <sub>2</sub> )	874	873			903	892	901	C-H wagging
A' (A <sub>1</sub> )	1003	994	1012	1008	975	1020	989	ip ring deformation
A' (B <sub>1</sub> )					981	1005	985	C-H wagging
A'' (B <sub>2</sub> )	974	975	968	970	997	989	999	C-C(Me)-H bending
A'' (A <sub>2</sub> )	997				1001	1007	1003	C-H wagging
A' (B <sub>1</sub> )	1042	1041			1068	1072	1068	C-C(Me)-H bending
A' (A <sub>1</sub> )	1070	1069	1064	1066	1076	1066	1074	ring C-H bending
A'' (B <sub>2</sub> )	1116				1107	1129	1113	ring C-H bending
A' (A <sub>1</sub> )	1225	1220			1232	1250	1238	ring C-H bending
A' (A <sub>1</sub> )	1212	1211	1214	1214	1236	1235	1231	ring C-H bending + C-Me stretching
A'' (B <sub>2</sub> )		1245			1284	1304	1290	ring stretching
A'' (B <sub>2</sub> )	1364				1351	1359	1350	ring C-H bending
A'' (B <sub>2</sub> )	1416	1414			1418	1438	1422	ring C-H bending
A' (A <sub>1</sub> )	1381	1378	1376	1375	1422	1427	1424	methyl umbrella motion
A'' (B <sub>2</sub> )	1446		1444	1450	1486	1477	1485	methyl bending
A' (A <sub>1</sub> )	1499	1496	1505		1489	1503	1494	ring C-H bending + ring stretching
A' (B <sub>1</sub> )	1456	1452			1493	1492	1493	methyl bending
A'' (B <sub>2</sub> )	1562	1563			1577	1564	1574	ring stretching
A' (A <sub>1</sub> )	1608	1604	1602	1610	1607	1624	1615	ring stretching

<sup>a</sup> The species refer to  $C_s$  symmetry; the classification of ref 5, according to  $C_{2v}$  pseudosymmetry, is reported in parentheses. SERS data in silver hydrosol are obtained at pH 6 (A) and at pH 11 (B). Wavenumbers are calculated for the free molecule (C), for the 4MePyAg<sup>+</sup> complex (D), and for the 4MePyAg<sup>0</sup> complex (E). <sup>b</sup> From ref 5.

instead, proposed an extension of the continuum polarizable model to compute the polarizability and its derivatives with respect to the atomic displacements for molecules physisorbed on metals. The substrate was described as a continuum acting as a perturbation on the adsorbed molecule, which was treated *ab initio*. Recently, density functional calculations have been also performed to obtain the structures and the vibrational properties of adsorbates treated as surface complexes, as for the chemisorption of phthalimide<sup>22</sup> 2-mercaptobenzoxazole<sup>23</sup> and pyrazolide.<sup>6</sup> Actually, the electromagnetic mechanism of the SERS effect is able to promote giant Raman enhancements (10<sup>6</sup> or more), much greater than those deriving from the chemical interaction between ligand and metal surface. In the first case, the SERS intensities are dependent on the resonance between the frequency of the plasmon wave of the metal particles and that of the exciting radiation. However, the simple model system, proposed here, constituted by a molecule of 4MePy bound to a single silver atom (Ag<sup>0</sup>) or ion (Ag<sup>+</sup>) cannot take into account the plasmon waves due to the excitation of the conduction electrons localized onto the metal surface. Although the enhancement factor due to the chemical effect is at most 10<sup>2</sup>, its influence on the observed spectra can be substantial when the exciting line is in resonance with the charge-transfer band of the ligand-surface adduct. Hence, the present DFT approach based on the evaluations of the relative intensities of the surface complexes can offer the possibility of distinguishing between different adsorbed species.

In Table 2, the calculated frequencies are reported for the free molecule as well as for the 4MePyAg<sup>+</sup> and 4MePyAg<sup>0</sup> complexes, as surface adsorption models, by adopting the same

basis set in order to correctly compare the calculated frequency shifts with those observed in the SERS. Although the basis set is really quite limited, this approach satisfactorily reproduces the vibrational frequencies of the free molecule, matching the assignment proposed by Arenas et al.<sup>5</sup> on the basis of normal coordinate analysis with a refined force field, with only the methyl bending modes resulting to be overestimated. All the observed Raman bands belong to species A' by assuming  $C_s$  symmetry; in particular, the prominent bands belong to species A<sub>1</sub> by assuming  $C_{2v}$  pseudosymmetry. Moreover, the band calculated at 15 cm<sup>-1</sup> is correctly described as a quasi-free rotation of the methyl group, because the internal rotation is not hindered as expected. The normal mode calculations performed by Arenas et al.,<sup>5</sup> instead, attributed an imaginary value to this vibration. Also, the SERS bands are satisfactorily reproduced by the DFT calculations, but the identification of the adsorbed species at different pH values in silver colloids or at different electrode potentials in an electrochemical cell is not possible by considering only the calculated wavenumbers, whereas it can be proposed on the basis of the comparison between observed and calculated intensities, as shown in Table 3. The intensity variations, predicted on going from the positively charged complex 4MePyAg<sup>+</sup> to the neutral complex 4MePyAg<sup>0</sup>, correspond to those observed in the electrochemical cell by shifting the electrode potential from  $E = 0$  V (SCE) to more negative values or in silver hydrosol by passing from acidic to alkaline pH. Actually, at  $E = 0$  V, the surface of the silver electrode is positively charged, whereas the zero-charge potential is near the value  $E = -0.75$  V. Hence, in the first case, the molecule can be reasonably assumed to be bound to a surface

**TABLE 3: Calculated and Observed Intensities**

most intense Raman bands of the liquid (see Table 2)	SERS intensities silver electrode $E = 0.0$ V	SERS intensities silver electrode $E = -0.75$ V	calculated intensities 4MePyAg <sup>+</sup> complex	calculated intensities 4MePyAg <sup>0</sup> complex
514		62	2	31
802	264	86	250	33
994	145	141	34	116
1069	100	35	35	11
1211	195	103	244	39
1378	110	31	184	42
1604	100	100	100	100

Ag<sup>+</sup> ion and in the second case, instead, to a neutral silver atom. By inspection of Table 3, it can be observed that most SERS bands decrease in intensity when the metal surface becomes less positively charged, as well as the calculated intensities; the SERS band around 535 cm<sup>-1</sup>, instead, increases in intensity, as correctly predicted by the DFT calculations. This also proves the importance and the validity of the present DFT approach, which involves the calculation of the Raman intensities, for identifying the complexes formed on the metal surface. On the other hand, the possibility of distinction between the adsorbed species by observing the Ag–N stretching mode in the low-frequency region (around 200 cm<sup>-1</sup>) is ruled out by the overlapping of the Ag–Cl stretching mode in the same spectral region.

The two adsorbed species, the positively charged (4MePyAg<sup>+</sup>) and neutral (4MePyAg<sup>0</sup>) complexes, present different electronic configurations, as argued by the optimized structures and by the Mulliken charges obtained by the DFT calculations. Figure 2 depicts the possible interactions of 4MePy with Ag<sup>+</sup> and with Ag<sup>0</sup> along with the indication of the bond distances for the free molecule and the two surface complexes. No molecular orientation can be deduced by DFT calculations

**TABLE 4: Comparison between Observed and Calculated Frequency Shifts**

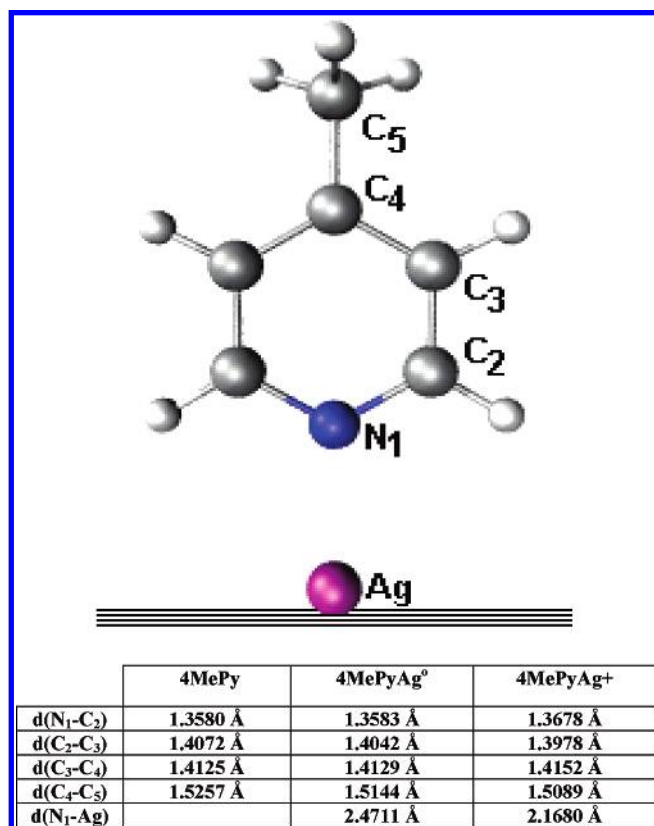
Raman bands of the liquid (see Table 2)	exptl $\Delta\nu$ liquid $\rightarrow$ colloid (pH 6)	exptl $\Delta\nu$ liquid $\rightarrow$ electrode ( $E = 0$ V)	calcd $\Delta\nu$ 4MePy $\rightarrow$ 4MePyAg <sup>+</sup>
485	+1		+3
514	+18		+34
670	-10		-6
802	+8	+6	+15
994	+18	+19	+30
975	-6		-8
1069	-5	-2	-10
1211	+3	+5	-1
1220		+11	+18
1378	-2	0	+5
1496	+9		+14
1604	-2	+2	+17

performed on simple models constituted by the molecule bound to a single metal adatom.

The neutral silver atom weakly interacts with the molecule, whose bond distances are little perturbed with respect to the free molecule. Thus, the Ag–N distance is quite long (2.47 Å) and a small negative charge,  $\sim 0.1 e$ , is transferred to the metal. In the case of interaction with a silver ion, instead, the charge transfer is larger,  $\sim 1/3 e$ , and the Ag–N bond distance is shorter (2.17 Å). The electronic structure of the molecule is strongly perturbed, as shown by the changes of the bond distances. In particular, the complex 4MePyAg<sup>+</sup> exhibits a tendency toward a pseudoquinonoid structure, because the C<sub>4</sub>–C<sub>5</sub> and C<sub>2</sub>–C<sub>3</sub> bond lengths are shortening but the N–C<sub>2</sub> and C<sub>3</sub>–C<sub>4</sub> bond lengths are lengthening. This, however, is not surprising, since the methyl group is an electron donor, whereas the silver ion, which is in the para position with respect to the methyl group, is electron withdrawing. The strong perturbation of the electronic distribution due to the interaction of the ligand with the positively charged silver surface gives rise to significant frequency shifts, which are also well reproduced by the DFT calculations for most SERS bands (Table 4).

## Conclusions

The band intensities observed in the Raman spectra of ligands adsorbed on SERS-active substrates are closely dependent on the enhancement mechanisms. The electromagnetic effect causes huge intensification of the SERS spectrum, where the relative intensities are related to the surface selection rules.<sup>24,25</sup> The molecules are considered physisorbed onto isolated metal particles with small average sizes with respect to the wavelength of the incident electromagnetic radiation. Even if the electromagnetic effect is generally the predominant mechanism in the SERS enhancement, also the “chemical effect” is to be taken into account, as pointed out in other cases.<sup>6,7,22,23,26,27</sup> In fact, when a molecule is chemisorbed on a metal, a surface complex is formed with significant changes in both the positions and intensities of the SERS bands with respect to the corresponding



**Figure 2.** Optimized structures of 4-methylpyridine and of its surface silver complexes, with indication of the corresponding bond distances. In the figure, no reference to the charge of the complexes is made.



ones in the normal Raman spectrum. The chemical effect is quite important in the SERS spectra of compounds adsorbed on silver colloids activated by the coadsorption of chloride anions, since the latter are able to promote an efficient charge-transfer effect between ligand and surface.<sup>28</sup> In the case of 4MePy adsorbed on silver colloids as well as on silver electrodes, the presence of coadsorbed chloride anions ensures an efficient charge-transfer effect, which affects both SERS frequencies and intensities. Actually, 4MePy is to be considered strongly chemisorbed on silver, as shown by the observed frequency shifts reported in Table 4. This justifies the present DFT calculation approach, based on surface complexes constituted by ligand molecules bound to surface adatoms like silver ions or neutral silver atoms. A strong charge-transfer interaction between molecule and metal, characterized by a pseudoquinonoid structure of the adsorbed species, is present when the silver surface is positively charged, as occurs in an electrochemical cell at electrode potentials near  $E = 0$  V or in silver hydrosols at an acidic pH. This study shows how the DFT method, albeit applied to simple molecule/metal interaction models, is able to predict the SERS spectra of ligands adsorbed on different silver substrates on the basis of the charge-transfer effect and the perturbation of the molecular structure.

Finally, a close correspondence is found between the SERS data of 4MePy adsorbed on silver colloids and silver electrodes, mainly concerning the relative intensities. Hydroxide anions, coadsorbed onto the silver particles in the colloidal suspension, play a role in making the metal surface negative as well as making the electrode potential shift to negative values in the electrochemical cell.

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