Theor Chem Acc (2007) 117:451–458
DOI 10.1007/s00214-006-0176-3

REGULAR ARTICLE

A density functional study of the SERS spectra of pyridine adsorbed on silver clusters

Gianni Cardini · **Maurizio Muniz-Miranda** ·
Marco Pagliai · **Vincenzo Schettino**

Received: 24 July 2006 / Accepted: 1 September 2006 / Published online: 31 October 2006

Abstract The effect of binding pyridine to silver clusters has been studied by density functional calculations by adopting a hybrid functional. The calculations allow proposing an explanation for the different SERS spectra of the ligand observed on Ag colloids in the presence and in the absence of coadsorbed chloride anions. In the latter case, a better agreement is obtained modeling the system by adsorption of pyridine on a $(Ag_4)^{+2}$ surface cluster.

Keywords DFT · SERS · Colloid · Silver · Pyridine · Chloride

1 Introduction

The SERS spectra of pyridine adsorbed on silver colloids strongly depend on many experimental conditions like sol preparation and aging. The addition of halide anions like chloride and bromide, which are strongly adsorbed on silver, improves the SERS enhancement giving rise to positively charged atoms onto the metal surface [1]. Hence, the formation of surface complexes, quite similar to coordination compounds, was observed [2–4]. In Ag hydrosols, activated by coadsorbed chloride anions, the presence of a pyridine/Ag^+ complex has been proposed on the basis of density functional theory (DFT) calculations [5,6]. Pyridine is strongly affected by the charge transfer between ligand and metal, showing a SERS spectrum with marked changes with respect to that observed in Ag hydrosol without halide anions. The differences in the two SERS spectra mainly concern the band intensities, as shown in Fig. 1. In salt-free Ag colloid, the ring breathing vibration at 1,008 cm^{-1} is weaker than the ring trigonal deformation at 1,036 cm^{-1}, as first observed by Creighton et al. [7]. By adding chloride ions the relative intensities are reversed, showing the same spectral pattern usually observed in the SERS of pyridine adsorbed on silver electrode with KCl electrolyte [8,9]. This suggests that the SERS intensity changes are related to the presence of chloride ions onto the silver surface. A possible explanation lies in the variation of the surface charge that could be induced by the coadsorption of chloride ions. By observing the different SERS spectra shown in Fig. 1, other two doublets, at 620–650 and at 1,570–1,600 cm^{-1}, exhibit reversed intensities. The purpose of this paper is to explain this spectral evidence by means of DFT calculations, performed for different adsorption models of pyridine on silver. This procedure has been successfully applied to the interpretation of the SERS of pyridine adsorbed on colloidal silver in the presence of chloride ions [5]. The previously adopted model consisted in a single silver ion bound to a neutral molecule of pyridine, but it could be necessary to take into account more complex models, based on silver clusters, to interpret the SERS of pyridine in salt-free Ag hydrosols. Silver clusters can be considered surface active sites [10,11], able to promote Raman enhancement by formation of molecule/metal complexes. A useful starting point is represented by the $(Ag_4)^+$ cluster, proposed by Roy and Furtak [12], like active site for the adsorption of pyridine. However, the formation of a double charged surface cluster like $(Ag_4)^{+2}$ is also

---

G. Cardini (✉) · M. Muniz-Miranda · M. Pagliai · V. Schettino
Dipartimento di Chimica, Universitá di Firenze,
Florence, Italy
e-mail: gianni.cardini@unifi.it

G. Cardini · V. Schettino
European Laboratory for Nonlinear Spectroscopy (LENS),
Polo Scientifico, Sesto Fiorentino 50019, Italy

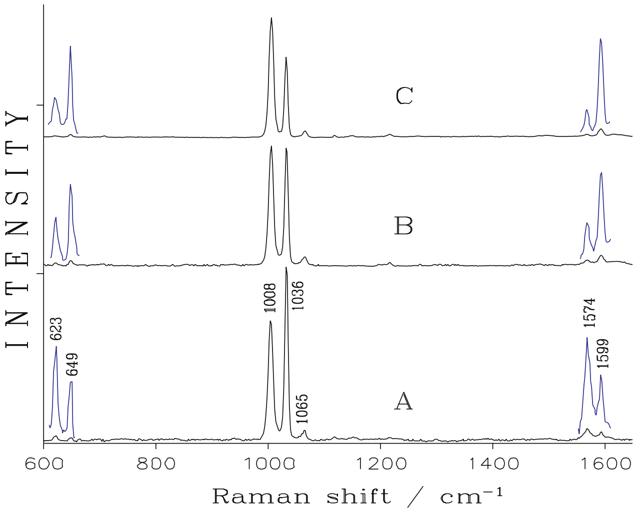

Fig. 1 SERS spectra of 5×10^{-3} M pyridine in salt-free Ag hydrosol (*A*) and in Ag hydrosols with 5×10^{-4} M NaCl (*B*) and with 5×10^{-3} M NaCl (*C*). Laser excitation line: 514.5 nm

possible during the reduction procedure of the silver ions, in colloids or at electrodes roughened by oxidation–reduction cycles (ORCs), accordingly to the following mechanism [13,14]:

$$Ag^+ + e^- \rightarrow Ag^o \tag{1}$$

$$Ag^o + Ag^+ \rightarrow (Ag_2)^+ \tag{2}$$

$$2(Ag_2)^+ \rightarrow (Ag_4)^{+2} \tag{3}$$

The use of the DFT to model silver clusters represents an attempt to describe the structural and dynamic properties of the Ag clusters, present in colloids as well as on roughened electrode surfaces, along with their ability to interact electronically with the ligand molecules. The binding energies of pyridine bound to neutral M_n (M = Cu, Ag, Au; $n = 2$–4) metal clusters were obtained and analyzed in terms of low-lying states and excited charge-transfer states by Wu et al. [15]. The same authors proposed a quantum chemical study of the interaction between pyridine and neutral metal clusters in terms of vibrational frequencies, by comparing different calculation procedures [16]. More recently, a detailed analysis of the interaction of pyridine with a silver surface was performed using time-dependent DFT for a model system of the ligand bound to a fragment of the bulk silver lattice constituted by 20 atoms [17]. This approach, however, did not consider the presence of positively charged Ag clusters, which are essential to the SERS signal of adsorbates in colloidal suspensions or in electrochemical cells.

In the present work, the properties of pyridine/silver complexes have been investigated by DFT calculations by considering silver ion clusters as active sites for the adsorption of the ligand on the metal surface. Ab initio calculations of pyridine adsorbed on Ag^+ model clusters allowed explaining the SERS frequency shifts observed at silver electrode [11]. Here, the calculated intensities of pyridine/silver clusters have also been obtained and compared with the SERS intensities observed in Ag hydrosols, with and without coadsorbed chloride anions. Actually, the SERS enhancements of the Raman bands of an adsorbate depend on both electromagnetic and chemical mechanisms [18]. But, in the case of pyridine adsorbed on Ag colloids, in the presence as well as in the absence of chloride anions, the molecule/surface chemical interaction undoubtedly plays an important role in the adsorption and, consequently, in the SERS effect, as evidenced by the significant frequency shifts with respect to the bands observed in the normal Raman spectra and the occurrence of Ag–N stretching bands in the low-frequency SERS spectra [5,19]. In addition, our previous investigation [5] evidenced that the effect of the electromagnetic mechanism on the SERS intensities weakens when the laser exciting line is far from resonance with the secondary surface plasmon band of the silver nanoparticles. When pyridine is adsorbed on chloride-free Ag colloid, this secondary plasmon band occurs at about 645 nm [6], whereas the SERS spectra are here obtained by excitation with the 514.5-nm laser line.

The present DFT calculations are performed on model systems where pyridine is bound to metal clusters constituted by four silver atoms with various positive charges. This modelization, which could seem too crude for mimicking the silver surface, should be suitable, instead, for representing the surface active sites where the ligand is really chemisorbed. Actually, these active sites are called “adatoms” or adclusters” because they are formed by one or few silver atoms, relatively isolated from the bulk metal and activated by the presence of positive charges. Hence, our study of the structural and vibrational properties of surface complexes of pyridine bound to silver ion clusters represent a reasonable attempt to improve the adsorption models previously proposed [5], and could offer a suitable approach for interpreting all the experimental data obtained in Ag colloids with or without coadsorbed chloride anions, including positions and relative intensities of the SERS bands.

2 Experimental

Stable Ag hydrosols were prepared according to Creighton’s procedure [7] and aged a week to prevent the formation of reduction products [20]. Then, NaCl and/or pyridine were added to the silver colloids. Ag(I)(pyridine)$_2$NO$_3$ was prepared by dissolving AgNO$_3$ in hot pyridine in the 1:2 molar ratio, according to Cooney's procedure [21].

Raman measurements were performed by using a Jobin-Yvon HG-2S monochromator, a cooled RCA-C31034A photomultiplier and a data acquisition facility. SERS data were obtained with the 514.5 nm exciting line supplied by an Ar$^+$ laser with a power of 50 mW. The Raman spectrum of the Ag(I)–pyridine coordination compound, as solid sample, was measured by using a defocused laser beam and a rotating device to avoid thermal effects.

3 Calculation method

All ab initio calculations have been performed by the Gaussian 98 package [22], adopting the B3LYP hybrid exchange correlation functional [23,24], along with the Lanl2DZ basis set. This latter consists of the Dunning/Huzinaga full double zeta [25] on first row atoms and of Los Alamos pseudopotential for core electrons plus a double zeta basis for valence electrons [26–28]. The structures were optimized with a *tight* criterion and the harmonic frequencies were calculated using an improved grid in the calculation of the integrals [Integral(Grid = 199,974)], with 0.98 scaling factor.

The Raman intensities of the vibrational modes, computed on the basis of the double harmonic approximation, i.e., without taking into account the electric and mechanical anharmonicities, correspond to spatially averaged values according to the usual formula reported in standard textbooks [29]:

$$I_{\mathrm{Raman}} \propto 45\underline{\alpha}^2 + 7\gamma^2$$

$$\underline{\alpha} = (1/3)\left[(\partial\alpha_{xx}/\partial Q_{k})_{\mathrm{o}} + (\partial\alpha_{yy}/\partial Q_{k})_{\mathrm{o}} + (\partial\alpha_{zz}/\partial Q_{k})_{\mathrm{o}}\right]$$

$$\begin{aligned}\gamma^2 = (1/2)\Big\{&\left[(\partial\alpha_{xx}/\partial Q_{k})_{\mathrm{o}} - (\partial\alpha_{yy}/\partial Q_{k})_{\mathrm{o}}\right]^2\\ &+\left[(\partial\alpha_{yy}/\partial Q_{k})_{\mathrm{o}} - (\partial\alpha_{zz}/\partial Q_{k})_{\mathrm{o}}\right]^2\\ &+\left[(\partial\alpha_{zz}/\partial Q_{k})_{\mathrm{o}} - (\partial\alpha_{xx}/\partial Q_{k})_{\mathrm{o}}\right]^2\Big\}\end{aligned}$$

The derivatives of the molecular polarizability with respect to the atomic displacements are considered as a response to an applied external electric field of 0.00189 a.u. Hence, the intensities depend only on the variation of the molecular polarizability due to the molecular vibration or rotation.

4 Results

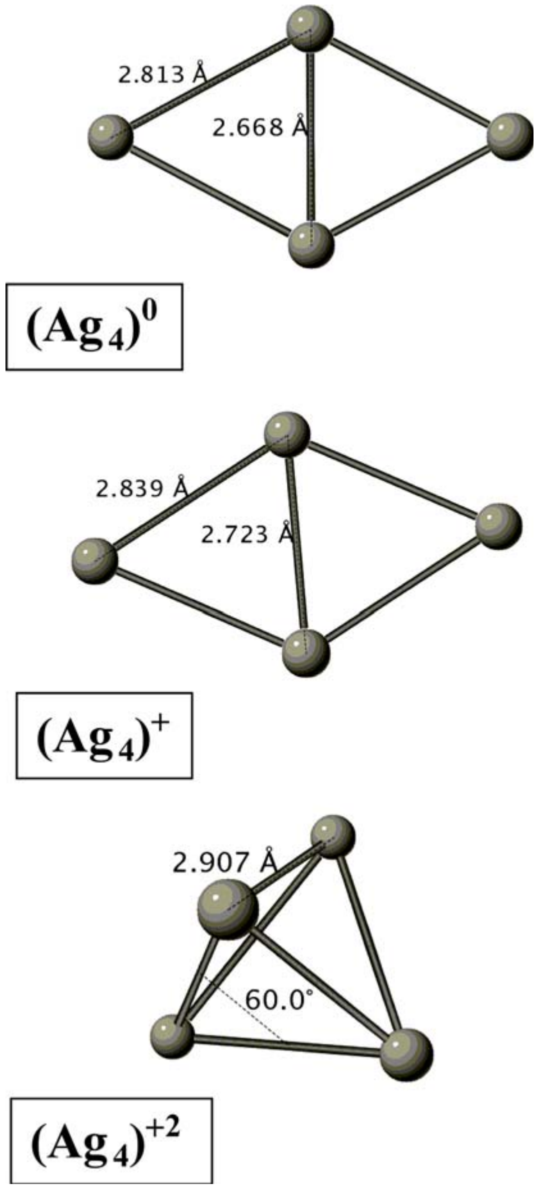

Fig. 2 Optimized structures of silver clusters

First, we want to check the reliability of clusters with four silver atoms in reproducing the Raman bands observed in the low-frequency region, for Ag hydrosols with or without chloride anions. In the 50–300 cm^{-1} spectral range, the bands related to the vibrational motions of silver clusters occur, along with those due to Ag–ligand vibrations. Hence, Ag clusters constituted by four atoms with 0 or +1 or +2 net charge have been examined with and without the presence of a chloride ion. Without chloride ion, stable rhombic structures are obtained for $(Ag_4)^+$ and $(Ag_4)^o$, while the optimized structure of $(Ag_4)^{+2}$ is tetrahedral (Fig. 2). The normal modes, reported in Table 1 for all the optimized structures, can be satisfactorily compared with the low-frequency Raman bands of chloride-free colloids, where only two broad bands are detected at about 70 and

Table 1 Calculated frequencies of silver clusters compared with the SERS frequencies

$(Ag_4)^+$ rhombic		$(Ag_4)^{+2}$ tetrahedral		$(Ag_4)^o$ rhombic		SERS[a]
Species	$\nu_{calc.}$	Species	$\nu_{calc.}$	Species	$\nu_{calc.}$	ν_{obs}
A_u	18	E	67	A_u	34	
B_u	69	E	67	B_u	67	
A_g	81	T_2	83	A_g	74	70
A_g	85	T_2	83	A_g	97	
B_u	122	T_2	83	B_u	146	
A_g	157	A_1	138	A_g	172	160

[a] In chloride-free Ag colloid

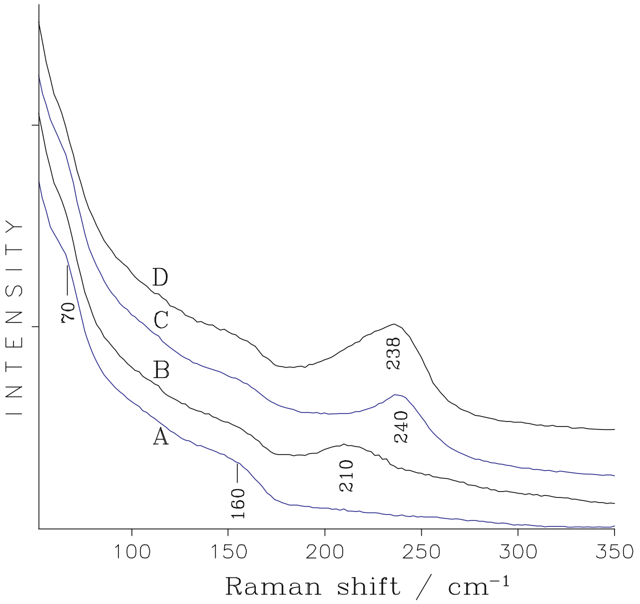

Fig. 3 Low-frequency SERS spectra of silver hydrosols. *A* Salt-free colloid without ligand; *B* salt-free colloid with 5×10^{-3} M pyridine; *C* colloid with 5×10^{-4} M NaCl; *D* colloid with 5×10^{-3} M pyridine and 5×10^{-4} M NaCl. Laser excitation line: 514.5 nm

160 cm^{-1} (Fig. 3A). In particular, the latter band can be related to the Debye frequency of solid silver occurring at 156 cm^{-1}, as previously proposed [30]. In Ag colloids with addition of chloride anions the same bands are observed, along with a strong band at 240 cm^{-1} attributable to the Ag–Cl stretching vibration (Fig. 3C). These bands correspond to those observed by Roy and Furtak on roughened Ag electrode with KCl as electrolyte, where also another weak band was detected at about 110 cm^{-1} [12]. By the adsorption of pyridine on chloride-free colloid, a SERS band at 210 cm^{-1} (Fig. 3B) is observed, attributable to Ag–N stretching vibration. When both pyridine and chloride ions are present in the Ag hydrosol, only one band with asymmetric structure occurs at 238 cm^{-1} (Fig. 3D), due to the overlapping of the Ag–N and Ag–Cl stretching vibrations.

By applying DFT calculations to metal clusters bound to a chloride ion, stable structures are obtained for $(Ag_4)^+Cl^-$ and $(Ag_4)^oCl^-$ complexes in pseudo-rhombic arrangements and for $(Ag_4)^{+2}Cl^-$ complex in a pyramidal arrangement (Fig. 4). The chloride anion results bound to $(Ag_4)^o$, $(Ag_4)^+$ $(Ag_4)^{+2}$ as monodentate, bidentate and tridentate ligand, respectively. On the basis of the calculated frequencies reported in Table 2, the presence of the $(Ag_4)^o$ cluster bound to a chloride ion can be ruled out, because the calculated Ag–Cl stretching mode is too high with respect to the corresponding band observed in the SERS spectrum at about 240 cm^{-1}, whereas the bands observed at about 70 and 110 cm^{-1} are underestimated. $(Ag_4)^+Cl^-$ and $(Ag_4)^{+2}Cl^-$ complexes are, instead, more probable. Actually, a mean deviation of 13.8 cm^{-1} is obtained for the neutral silver cluster, whereas a mean deviation of 8.2 cm^{-1} for the two other clusters.

The same silver clusters, $(Ag_4)^+$ and $(Ag_4)^{+2}$, can be taken into consideration for the DFT calculations as surface active sites for the adsorption of a ligand like pyridine (hereafter Py). Py results bound to a $(Ag_4)^+$ pseudo-rhombic cluster or to a $(Ag_4)^{+2}$ pyramidal cluster, as shown in Fig. 5. The calculated normal modes are reported in Table 3 with the corresponding Raman intensities, in comparison with the SERS frequencies and intensities. Our previous calculations [5] for pyridine bound to a single Ag^+ ion were able to reproduce satisfactorily both band positions and intensities when compared to the SERS of pyridine adsorbed on silver colloid in the presence of chloride ions. Now, by considering pyridine bound to the $(Ag_4)^+$ cluster, a little worse agreement is obtained, with 8.0 cm^{-1} mean deviation instead of 7.2 cm^{-1}; e.g., the ring-breathing mode downshifts to 996 cm^{-1} with respect to the observed value at 1008 cm^{-1} and the Ag–N stretching mode to 197 cm^{-1}, instead of 210 cm^{-1}, as experimentally found (Fig. 3). It is also interesting to check the behavior of the calculated intensities in the 1,000–1,050 cm^{-1} spectral region: on going from Py/Ag^+ to Py/$(Ag_4)^+$, the ring trigonal deformation mode strongly decreases in intensity with respect to the ring breathing mode, in contrast with the experimental findings. The Py/$(Ag_4)^+$ model complex can be considered therefore less able to

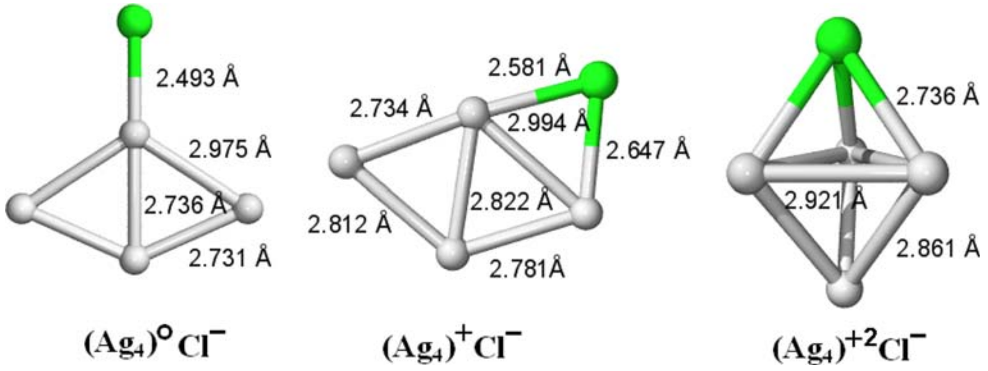

Fig. 4 Optimized structures of silver/chloride clusters

Table 2 Calculated frequencies of silver clusters bound to a chloride ion, compared with the SERS frequencies

$(Ag_4)^+Cl^-$ pseudo-rhombic $\nu_{calc.}$	$(Ag_4)^{+2}Cl^-$pyramidal $\nu_{calc.}$	$(Ag_4)^oCl^-$ pseudo-rhombic $\nu_{calc.}$	SERS[a] ν_{obs}
23	62	28	
45	62	41	
58	76	53	
78	76	54	70
99	87	57	
126	107	95	110[b]
136	107	145	
159	143	158	160
248	243	262	240

[a] In Ag colloid with chloride anions
[b] At Ag electrode [12]

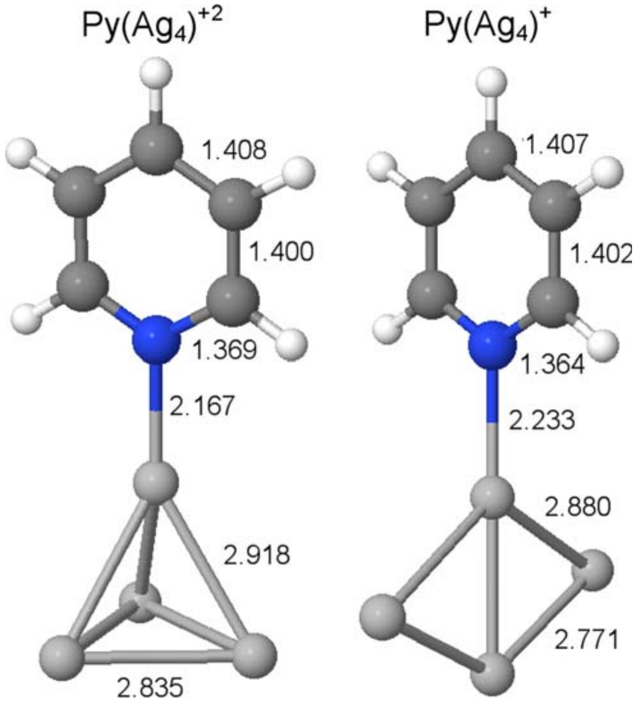

Fig. 5 Optimized structures of pyridine bonded to silver clusters

predict the SERS intensities of pyridine in Ag/Cl− colloid. A further attempt of improving the results was also done by considering pyridine bound to a neutral silver cluster, $(Ag_4)^o$, but in this case a marked downshift is calculated for the ring-breathing mode (calc. 996 cm^{-1}) as well as for the Ag–N stretching mode (calc. 194 cm^{-1}). Moreover, the ratio between the calculated intensities of the ring trigonal deformation and of the ring breathing mode becomes 1:4, in contrast with the experimental findings. This confirms the conclusions of the previous work [5], that in Ag hydrosols with coadsorbed chloride anions the species responsible of the SERS is suitably modeled by a single silver ion bound to pyridine, closely resembling the Ag(I)–pyridine coordination compound, whose Raman spectrum is reported for comparison in Fig. 6. In fact, the adsorption of chloride anions on Ag colloidal particles induces the formation of surface Ag^+ ions [1]; hence, pyridine molecules react with these active sites by forming σ-bonds with the silver ions *via* the nonbonding electron pairs (n^2) on the N atoms, very much like to what found in the coordination complexes [31].

The SERS of pyridine in salt-free silver colloid, instead, is well reproduced only by DFT calculations performed for pyridine bound to a $(Ag_4)^{+2}$ pyramidal cluster. In the low-frequency region the Ag–N stretching mode is calculated at 213 cm^{-1}, in close agreement with the experimental value at 210 cm^{-1} (see Fig. 3). The strongest vibration is not the ring breathing mode anymore, but the ring trigonal deformation, in close

Table 3 Calculated frequencies of pyridine/silver complexes compared with the SERS frequencies observed in Ag colloids (Calculated relative Raman intensities reported in parentheses)

Species	Py/$(Ag_4)^{+2}$ Calc.	Py/$(Ag_4)^{+}$ Calc.	Py/Ag^{+} Calc.	Py on Ag, colloid I Obs. SERS	Py on Ag, colloid II Obs. SERS
(Ag–N)	213 (4.2)	197 (12.1)	201 (5.6)	210 br	(238)[a]
A_2	392 (0.2)	391 (0.2)	392 (0.2)		
B_1	425 (0.2)	427 (0.0)	427 (0.6)		416 vw
A_1	644 (29.4)	636 (2.6)	644 (10.2)	623 m	623 w
B_2	649 (11.0)	652 (7.3)	649 (14.2)	649 w	649 m
B_1	708 (0.0)	714 (0.1)	708 (0.9)		708 vw
B_1	772 (1.2)	770 (0.3)	771 (2.4)		
A_2	889 (0.1)	897 (0.2)	892 (0.1)		
B_1	962 (1.0)	961 (0.7)	963 (0.6)	942 vw	942 vw
A_1	997 (100.0)	996 (100.0)	1,000 (100.0)	1,008 vs	1,008 vvs
A_2	1,004 (0.1)	1,003 (0.4)	1,004 (0.1)		
A_1	1,039 (190.4)	1,036 (27.9)	1,038 (88.4)	1,036 vvs	1,036 vs
B_1	1,046 (0.0)	1,040 (0.0)	1,044 (0.0)		
B_2	1,065 (1.0)	1,067 (4.2)	1,077 (1.4)		
A_1	1,076 (0.8)	1,073 (0.1)	1,067 (0.5)	1,065 m	1,065 m
B_2	1,191 (3.9)	1,191 (3.9)	1,189 (4.7)	1,199 vw	1,199 vw
A_1	1,230 (17.7)	1,229 (11.0)	1,232 (11.1)	1,221 w	1,221 w
B_2	1,298 (0.2)	1,292 (0.0)	1,295 (0.1)	1,298 vw	
B_2	1,372 (1.3)	1,372 (0.3)	1,373 (2.2)		1,376 vw
B_2	1,453 (2.2)	1,451 (0.6)	1,454 (1.4)		
A_1	1,479 (2.4)	1,480 (3.0)	1,480 (2.2)		1,486 vw
B_2	1,574 (20.4)	1,579 (12.6)	1,578 (26.2)	1,574 m	1,574 w
A_1	1,603 (24.3)	1,605 (41.4)	1,606 (34.7)	1,599 w	1,599 m

Symmetry species referred to pyridine; *colloid I* without chloride anions, *colloid II* with chloride anions

[a] Overlapping of Ag–N and Ag–Cl stretching vibrations

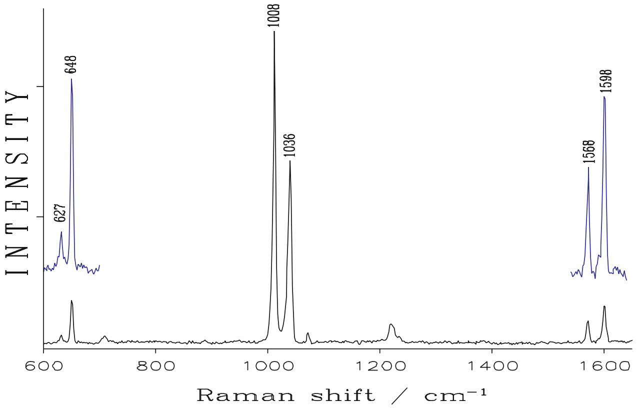

Fig. 6 Raman spectrum of the Ag(I)–pyridine coordination compound. Laser excitation line: 514.5 nm

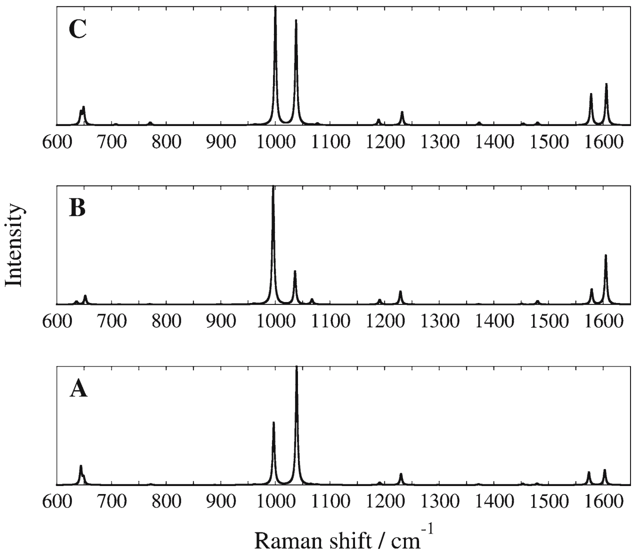

Fig. 7 Calculated SERS spectra of pyridine bound to silver clusters: $(Ag_4)^{+2}$ (*A*); $(Ag_4)^{+}$ (*B*); and Ag^{+} (*C*)

analogy with findings in Ag colloids without chloride ions (Fig. 1A). A similar intensity inversion is observed for the doublet at 620–650 cm^{-1}; moreover, in the high-frequency region the C=C stretching mode calculated around 1,600 cm^{-1} becomes weaker, as experimentally observed. Hence, in the absence of coadsorbed halide anions, pyridine can be considered as bound to a pyramidal silver cluster, as previously suggested by Roy and Furtak [12], but with a doubly positive charge.

The visual comparison between the calculated Raman spectra of pyridine bound to Ag^{+}, $(Ag_4)^{+}$ and $(Ag_4)^{+2}$ is reported in Fig. 7, where the bands are shown as Lorentzian shapes having 4-cm^{-1} bandwidths.

5 Discussion and conclusions

On the basis of DFT calculations, the formation of silver clusters on Ag colloidal particles has been analyzed and the SERS spectra of pyridine adsorbed on silver have been interpreted by explaining the different intensity pattern observed in the presence and in the absence of chloride anions. Actually, the validity of this method to investigate the adsorption of a ligand on silver lies in correctly reproducing both SERS frequencies and intensities. Recently [32], *ab-initio* calculations on a Hartree–Fock level, performed on Py/Ag^+ or Py/$(Ag_5)^+$ model system, did not successfully reproduce the SERS relative intensities. The present DFT approach, which considers clusters with four silver atoms and different positive charges, is able, instead, to describe satisfactorily the SERS spectra of pyridine. Hence, it represents a valid attempt to mimic the effect of the surface active sites by the interaction of the metal electrons with the electronic distribution of the molecule.

Two different pyridine/metal surface complexes are here proposed: in Ag colloids with chloride anions, the adsorbate closely resembles the ligand in the Ag(I) coordination compound; in salt-free colloids, instead, the pyridine molecules can be modeled as chemisorbed onto $(Ag_4)^{+2}$ pyramidal clusters like surface active sites. This finding can be extended to the behavior of pyridine adsorbed on silver electrode as a function of the applied electrode potential. Two different explanations were proposed for the role of the chloride ions in the charge transfer between molecule and silver substrate. Hildebrand et al. [33] suggested that the role of chemisorbed anions like Cl^- or Br^- is to promote positively charged SERS-active sites. Henglein et al. [34], instead, proposed a change in the electron density on the colloid surface when nucleophilic ligands, as for example chloride anions, are adsorbed on silver, by varying the Fermi level position of the metal nanoparticles, in close analogy to what happens by changing the electrode potential in an electrochemical cell. Actually, the position of the Fermi level of an electrode is controlled by a potentiostat, whereas in a metal hydrosol this level can float upon chemisorption of nucleophiles [35]. Hence, the SERS spectra obtained from Ag colloids can be compared with those from electrode. A detailed analysis of the SERS spectra of pyridine in an electrochemical cell has been reported by Arenas et al. [8], taking Ag/AgCl/KCl electrode as reference. At negative electrode potentials, but more positive with respect to the zero-charge potential ($E \sim -0.75$ V), the SERS corresponds to that observed in Ag/Cl^- colloid. At $E = 0$, when the surface is more positively charged, the SERS spectrum closely resembles the SERS of pyridine adsorbed on salt-free Ag colloid. This further supports the model here proposed, constituted by pyridine bound to a pyramidal silver cluster with doubly positive charge.

Some considerations can be done on the kind of interaction between ligand and substrate. On the basis of the Mulliken atomic charges, calculated by DFT method, the electron charge transfer from molecule to metal is evaluated as 1/3 *e* for both the Py/$(Ag_4)^{+2}$ and Py/Ag^+ species, which are considered the most probable in salt-free Ag colloid and in Ag colloid with chloride anions, respectively. The species Py/$(Ag_4)^+$, considered with lower probability, exhibits, instead, a smaller charge transfer, less than 1/4 *e*. Consequently, a strong chemical interaction between the molecule and the active sites of the silver surface can be proposed for the complexes Py/$(Ag_4)^{+2}$ and Py/Ag^+, as suggested also by the short Ag–N distances, 2.167 and 2.176 Å, respectively, whereas this distance is longer (2.233 Å) in the complex Py/$(Ag_4)^+$.

As a conclusion, the extension of the DFT calculations to metal clusters constituted by silver atoms with different charges represents an improvement of the previous model of pyridine interacting with the silver surface [5]. Actually, the goal of these calculations is to explain for the first time the chloride effect observed in the SERS spectra, by considering the modifications of the surface active sites induced by the coadsorption of Cl^- anions, along with the structural changes of the ligand interacting with silver adclusters. The formation of the two different adsorbates in the absence and in the presence of coadsorbed chloride anions is closely related in both cases to strong charge-transfer effects between pyridine and active sites of the silver surface. These effects are evidenced by the decrease of the molecule–metal separation predicted by the DFT calculations.

Finally, some conclusive remarks can be outlined on the different mechanisms of the SERS effect in relation with the present theoretical approach. The SERS enhancement can be considered [36] as the product of two major contributions, an electromagnetic and a chemical mechanism, since the intensity of Raman scattering is directly proportional to the square of the induced dipole moment, which, in turn, is the product of the Raman polarizability and the magnitude of the incident electromagnetic field. By exciting the surface plasmon resonance of a nanostructured or nanoparticle metal surface, the local electromagnetic field, *E,* is enhanced by 10. Since Raman scattering approximately scales as E^4, the electromagnetic enhancement factor is of the order 10^4. Chemical enhancement includes any enhancement of the Raman intensity of the adsorbed molecules due to the chemical reaction with the surface and it is related to the charge transfer between ligand

and metal active sites. Two main types of charge transfer processes are possible. By interaction with the surface the polarizability of the molecule may increase with the redistribution of the charge in the electronic ground state, promoting different enhancements for different vibrational modes. This mainly occurs by formation of surface complexes between ligand and metal adatoms or adclusters. Another chemical enhancement mechanism depends on the photo-assisted charge transfer process when the incident laser energy matches the energy difference between the Fermi level of the metal substrate and the molecular HOMO or LUMO [37]. Albeit these chemical mechanisms can provide enhancement of the Raman signal of the adsorbate only up to 10^2, they significantly affect the SERS relative intensities when the wavelength of the laser exciting line is off-resonance with respect to the surface plasmon band of the metal nanoparticles [5], as in the present case of pyridine adsorbed on Ag colloids. Our theoretical approach takes into account only the chemical mechanism related to the polarizability changes in the electronic ground state of the pyridine/silver surface complexes. However, our modelization of the silver adclusters, which act as active sites for the adsorption of the ligand, is really able to correctly reproduce positions and relative intensities of the SERS bands of pyridine in Ag colloids, both in the presence and in the absence of coadsorbed chloride anions.

Acknowledgements The authors gratefully thank the Italian Ministero dell‘Istruzione, Universita’ e Ricerca (MIUR) and the Consiglio Nazionale delle Ricerche (CNR) for the financial support to the ≪Progetto Finalizzato Materiali Speciali II≫.

References

1. Muniz-Miranda M, Sbrana G (1996) J Raman Spectrosc 27:105
2. Sbrana G, Neto N, Muniz-Miranda M, Nocentini M (1990) J Phys Chem 94:3706
3. Neto N, Muniz-Miranda M, Sbrana G (1996) J Phys Chem 100:9911
4. Muniz-Miranda M (2000) J Phys Chem A 104:7803
5. Muniz-Miranda M, Cardini G, Schettino V (2004) Theor Chem Acc 111:264
6. Pagliai M, Bellucci L, Cardini G, Muniz-Miranda M, Schettino V (2006) Phys Chem Chem Phys 8:171
7. Creighton JA, Blatchford CG, Albrecht MG (1979) J Chem Soc Faraday Trans II 75:790
8. Arenas JF, López-Tocón I, Otero JC, Marcos JI (1996) J Phys Chem 100:9254
9. Li X-Y, Huang Q-J, Petrov VI, Xie Y-T, Luo Q, Yu X, Yan Y-J (2005) J Raman Spectrosc 36:555
10. Otto A, Billmann J, Eickmans J, Ertürk Ü, Pettenkofer C (1984) Surf Sci 138:319
11. Vivoni A, Birke RL, Foucault R, Lombardi JR (2003) J Phys Chem B 107:5547
12. Roy D, Furtak TE (1986) Phys Rev B 34:5111
13. Mulvaney P, Henglein A (1990) Chem Phys Lett 8:391
14. Ershov BG, Janata E, Henglein A (1993) J Phys Chem 97:339
15. Wu DY, Hayashi M, Chang CH, Liang KK, Lin SH (2003) J Chem Phys 118:4073
16. Wu DY, Hayashi M, Shiu YJ, Liang KK, Chang CH, Yeh YL, Lin SH (2003) J Phys Chem A 107:9658
17. Zhao L, Jensen L, Schatz GC (2006) J Am Chem Soc 128:2911
18. Otto A (1984) In: Cardona M, Güntherodt G (eds) Light Scattering in solids, Chapt. 6, vol IV. Springer, Berlin Heidelberg New York
19. Muniz-Miranda M (2001) Chem Phys Lett 340:437
20. Muniz-Miranda M, Neto N, Sbrana G (1986) J Mol Struct 143:275
21. Cooney RP, Howard MW,Mahoney MR (1981) Chem Phys Lett 79:459
22. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA Jr, Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Gonzalez C, Challacombe M, Gill PMW, Johnson BG, Chen W, Wong MW, Andres JL, Head-Gordon M, Replogle S, Pople JA (1998) Gaussian 98. Gaussian, Pittsburgh, PA
23. Becke AD (1988) Phys Rev A 33:3098
24. Lee C, Yang W, Parr RG (1988) Phys Rev B 37:785
25. Dunning TH Jr, Hay PJ (1976) In: Schaefer HF III (ed) Modern theoretical chemistry, vol 3, Plenum, New York, pp 1–27
26. Hay PJ, Wadt WR (1985) J Chem Phys 82:270
27. Wadt WR, Hay PJ (1985) J Chem Phys 82:284
28. Hay PJ, Wadt WR (1985) J Chem Phys 82:299
29. Wilson EB, Decius JC, Cross PC (eds) (1980) Molecular vibrations. Dover, New York
30. Bosnick KA, Haslett TL, Fedrigo S, Moskovits M, Chan W-T, Fournier R (1999) J Chem Phys 111:8867
31. Crosby GA (1983) J Chem Educ 60:791
32. Johansson P (2005) Phys Chem Chem Phys 7:475
33. Hildebrandt P, Stockburger M (1984) J Phys Chem 88:5935
34. Henglein A, Mulvaney P, Linnert T (1991) Faraday Discuss 92:31
35. Henglein A (1993) J Phys Chem 97:5457
36. Moskovits M (1985) Rev Mod Phys 57:783
37. Lombardi JR, Birke RL, Lu T, Xu J (1986) J Chem Phys 84:4174