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Adsorption Models of Bipyrazine on Silver Colloidal Nanoparticles: A Computational Study [#]

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Abstract

Motivation. The Surface Enhanced Raman Scattering (SERS) spectra of bipyrazine (BPZ) adsorbed on silver colloids display interesting spectral features. In fact, upon addition of NaCl to the colloid, some bands are split into doublets. This behavior can be explained with two different interactions of BPZ with the silver surface. In order to gain a better insight into the adsorption mechanism of BPZ on silver, Density Functional Theory (DFT) calculations of two models of the surface complexes of BPZ were performed.

Method. We have performed DFT calculations using the B3LYP functional and the LANL2DZ basis set.

Results. The B3LYP/LANL2DZ calculations of two models of the surface complex of BPZ ("*ortho*" and "*meta*") are able to account for the splitting of bands observed in the SERS spectra. In fact, the components of the SERS doublets can be assigned to normal modes of the two models of BPZ/Ag(I) surface complex.

Conclusions. The hypothesis of two different interactions of BPZ with the silver surface is confirmed by the B3LYP/LANL2DZ calculations of the two BPZ/Ag(I) models: a fraction of molecules adsorbs on silver through the *meta* nitrogen atom and the remaining part *via* the *ortho* nitrogen atom of BPZ. Thus, the splitting of the SERS bands is ascribed to the presence of both BPZ/Ag(I) complexes on the silver surface.

Keywords. Bipyrazine; adsorption models; DFT calculations; SERS; silver nanoparticles.

Abbreviations and notations

SERS, surface enhanced Raman scattering	DFT, density functional theory
RS, normal raman	BPZ, bipyrazine

1 INTRODUCTION

The Surface Enhanced Raman Scattering (SERS) effect is the enormous Raman intensity enhancement displayed by some molecules when adsorbed on rough metal substrates (usually coinage metals). This giant intensity enhancement (till 10^{14} in particular experimental conditions) has been explained with two main mechanisms: the electromagnetic [1] and the chemical [2].

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According to the first mechanism, the Raman enhancement of an adsorbed molecule is due to the resonance between the excitation wave of the electrons localized at the surface of a metal nanoparticle and the incident laser radiation. The electron plasma excitation induces an electric field near the metal particle much stronger than that far from the surface, with a consequent strong increase of the Raman signal of the adsorbate. According to the chemical effect, instead, the molecular polarizability is hugely increased upon adsorption on the metal surface due to the charge transfer between the molecule and metal.

When the chemical mechanism plays a significant role in the SERS effect, the molecule is "chemisorbed" on the metal surface. In this case a surface complex is formed and, on going from the normal Raman (RS, hereafter) to the SERS spectra, some bands can undergo considerable shifts to lower or higher wavenumbers. These wavenumber shifts can be ascribed to the noticeable changes undergone by some force constants of the free molecule, upon binding to the metal surface. Therefore, these wavenumber shifts can be used for the evaluation of the contribution of the chemical effect to the SERS enhancement.

Density Functional Theory (DFT) calculations are a powerful tool to get a better insight into the chemisorption mechanism of molecules on metal surfaces [3,4,5]. In particular, useful information can be obtained from the calculations of the wavenumbers and the related normal modes of vibrations of reliable models of the molecular adsorption on the metal surface. In order to evaluate the reliability of models, calculated wavenumbers are to be obtained for several models of the molecule/metal complex and then compared to the experimental data. A molecule/metal interaction model can be considered reliable when provides a good agreement with the experimental wavenumbers.

A computational investigation on the adsorption mechanism of bipyrazine (BPZ hereafter) in Ag hydrosols is here reported. This compound is chemisorbed on the silver surface, therefore its adsorption can be mimicked by models of the BPZ/Ag(I) surface complex. Upon addition of NaCl to the system constituted by BPZ and silver colloid, the occurrence of splitting of some bands is observed. This evidence was considered diagnostic of the formation of two different BPZ/Ag(I) surface complexes [6], as interpreted with the help of normal mode calculations of BPZ/Ag(I) complexes, taking into account the vibrational assignment performed for the free molecule [7]. Nowadays, since those calculations are not considered sufficiently accurate, an improvement of the previous results by means of the computational DFT approach on the same models has been considered of interest. Thus, we performed DFT/B3LYP calculations with the LANL2DZ basis set for the two molecule/silver interaction models previously proposed [6], in order to obtain more accurate computational results for the investigation of the adsorption of BPZ on silver surfaces.

Table 1. SERS data and calculated wavenumbers for the "*ortho*" and "*meta*" models of BPZ/Ag(I)

$\tilde{\nu}_{\text{obs.}}$ [a]	$\tilde{\nu}_{\text{calc } ortho}$	$\tilde{\nu}_{\text{calc } meta}$
1595 sh	1585	1597
1590 s	1562	1577
1574 sh	1548	1556
1518 vs	1545	1549
1504 sh	1503	1505
1473 w	1468	1469
1451 w	1441	1450
1435 w	1413	1408
1404 vw	—	—
1365 vw	1349	1346
1333 vw	1332	1334
1316 s	—	—
1303 s	1307	1303
1258 vw	1244	1257
—	1231	1234
1216 w	1192	1189
1170 w	1174	1164
1151 w	1123	1120
1086 m	—	1074
1063 m	1065	—
—	1041	1040
1024 vs	1022	—
1017 vs	—	1012
—	1012	1012
—	1004	1009
972 vw	1000	1002
—	977	997
936 w	961	986
867 w	888	900
—	875	872
829 m	—	816
807 m	803	—
781 vw	799	789
752 vw	785	777
721 vw	710	712
695 vw	651	665
663 w	—	—
634 sh	618	621
613 sh	—	—
597 vw	590	604
573 vw	510	474
455 w	451	456
413 vw	438	437
—	360	381
357 vw	332	338
—	248	218
—	169	195
—	153	175
—	121	116
—	91	88
—	63	70
—	46	43

[a] From Ref. [6].

2 METHODS AND CALCULATIONS

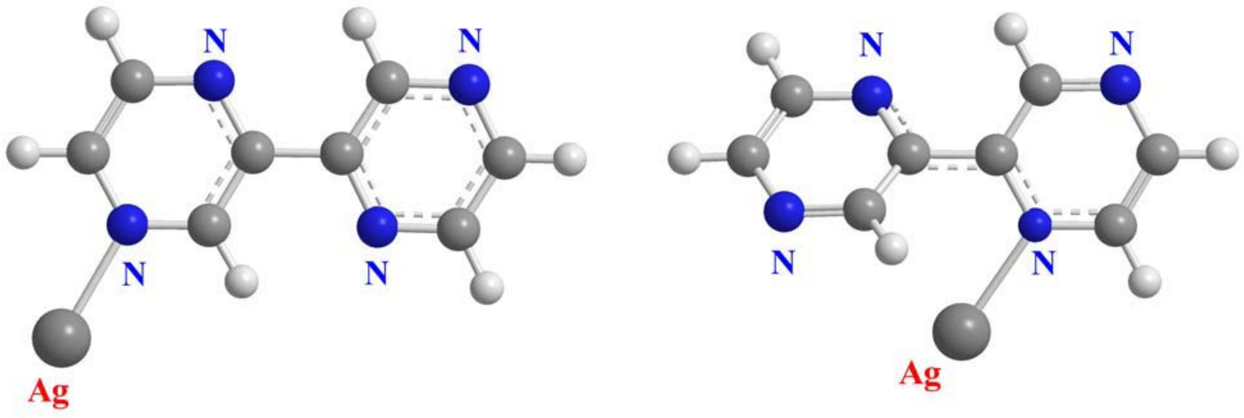
The calculations of BPZ/Ag(I) models with the molecule bound to a silver ion by interaction of a nitrogen atom in "*meta*" or in "*ortho*" position with respect the C–C inter–ring bond were carried out using GAUSSIAN 98 package [8]. The geometries were fully optimized at the density functional level of theory with the Becke 3–parameter hybrid functional combined with the Lee–Yang–Parr correlation functional (B3LYP). The LANL2DZ basis set was used for all the calculations.

By allowing that all the parameters could relax, the calculations converged to optimized geometries, which corresponded to true energy minima, as revealed by the lack of imaginary values in the vibrational mode calculations. The harmonic vibrational wavenumbers were calculated at the same level of approximation using the parameters corresponding to the structure obtained from the optimization step. Force constants in internal coordinate, which were calculated according to the procedure described elsewhere [9], were used for a standard zero–order GF–matrix treatment from which the vibrational wavenumbers and the Potential Energy Distributions (PEDs) were obtained. The table of the PEDs are not reported here, but it can provided by authors upon request. No scaling factors were applied to the calculated wavenumbers. SERS data, compared with the calculated results, are reported in Table 1.

3 RESULTS

3.1 Structure of Surface Complex Models

DFT calculations have been performed on models of BPZ bound to one Ag^+, since the surface Ag sites are to be considered positively charged by effect of coadsorbed halide anions [10,11]. The optimized structures of the two BPZ/Ag(I) conformers are reported in Figure 1.



"*Meta*" BPZ/Ag(I)

"*Ortho*" BPZ/Ag(I)

Figure 1. Optimized structures of surface complex models calculated at the B3LYP/LANL2DZ level.

The “*meta*” BPZ/Ag(I) is predicted to be in the coplanar conformation, which provides the largest π–electron conjugation, whereas the “*ortho*” conformer is twisted, due to the strong sterical repulsion between the silver ion bound to an aromatic ring and the *ortho* hydrogen atom of the other ring. Therefore, the symmetry of the *meta* conformer is C_s, whereas the *ortho* conformer has no symmetry.

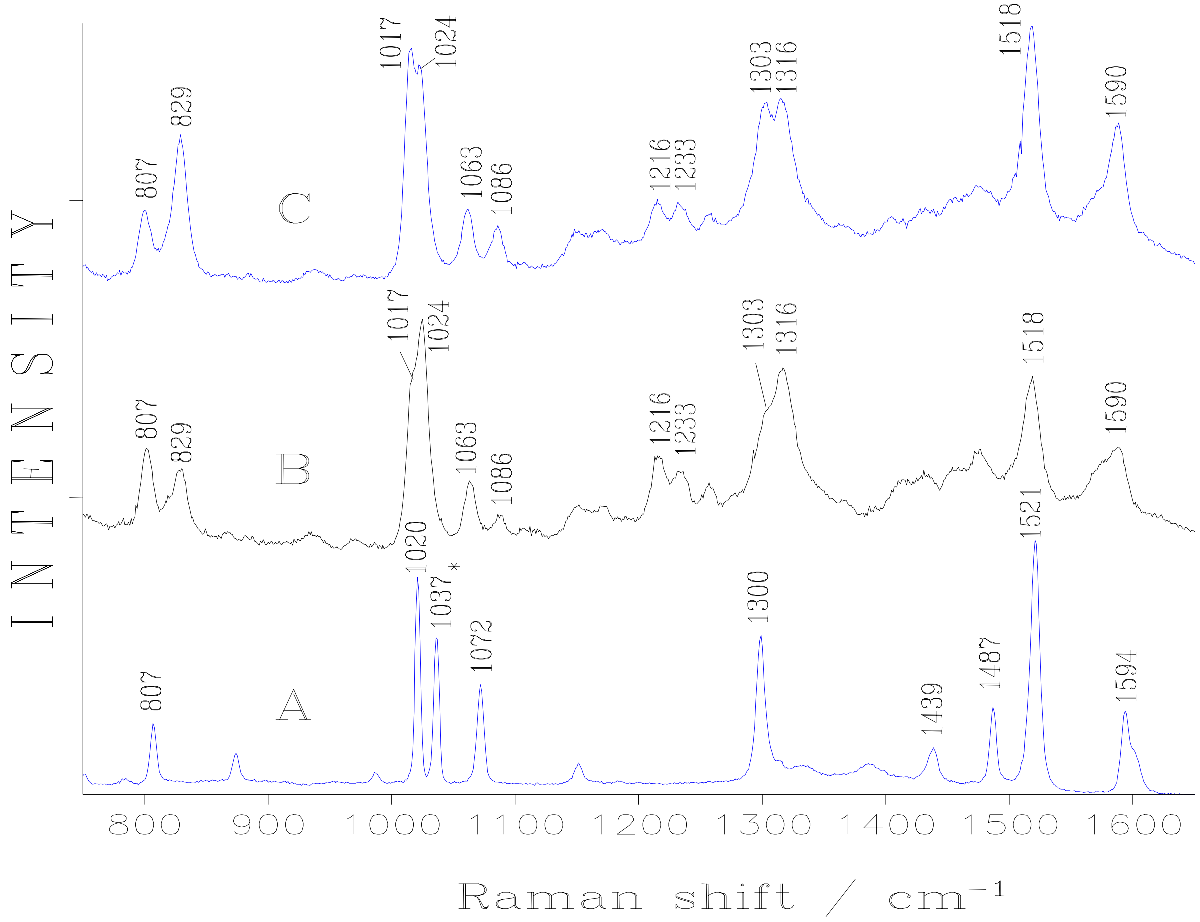


Figure 2. (A) Raman spectra of 1:1 BPZ/$AgNO_3$ coordination compound, the band marked by an asterisk corresponds to the totally symmetric stretching mode of the nitrate group; (B) and (C) SERS spectra of two different samples of BPZ adsorbed on Ag sols.

3.2 Interpretation of the SERS Spectra

Figure 2 shows the RS spectrum of $AgNO_3$/BPZ coordination compound and the SERS spectra of two samples of BPZ adsorbed on silver colloids. The RS spectrum of the coordination compound is similar to the SERS spectrum, even if the positions and relative intensities of some bands are different. Regarding the intensity, it is important to stress that in a SERS spectrum the intensity of bands mainly depends upon the electromagnetic mechanism, which is absent in the case of a RS spectrum. On the other hand, the different position of some bands in the SERS and in the RS spectra of the complex can be due to the different arrangement adopted by BPZ in the surface complex and in the coordination compound. In fact, in the latter, the silver ions and the molecules form a polymeric chain. The *cis*–planar conformation was excluded for the BPZ/Ag(I) coordination compound; thus, on the basis of the similarity between the SERS and RS spectrum of the complex, the adsorption of BPZ in a bidentate arrangement was also excluded. The SERS spectra display doublets at 807/829 cm^{-1}, 1017/1024 cm^{-1}, 1063/1086 cm^{-1} and 1303/1316 cm^{-1}. In particular, upon increasing of the relative intensity of the SERS band at 829 cm^{-1}, an intensity increase of the spectral features at 1017 and 1086 cm^{-1} was also observed. This spectral evidence was ascribed to an involvement of the *meta* nitrogen atom of BPZ in the interaction with the metal surface. On the other hand, the SERS bands at 807, 1024 and 1063 cm^{-1} were attributed to a different molecular adsorption: the interaction of BPZ *via* the *ortho* N atom. The doublet in the 1300 cm^{-1} region was interpreted with the presence of two different totally symmetric vibrational modes. Therefore the coexistence of two different interactions of BPZ with the metal surface was proposed: the "*ortho*" and the "*meta*" BPZ/Ag(I) complexes [6].

We carried out B3LYP calculation of the harmonic wavenumbers for the above–mentioned adsorption models. A good agreement between calculated and experimental data was obtained without using scaling factors for the calculated wavenumbers. The SERS bands at 1086, 1017 and 829 cm^{-1} are assigned to normal modes of the "*meta*" BPZ/Ag(I) complex, whereas the SERS bands at 1063, 1024 and 807 cm^{-1} are attributed to normal modes of the "*ortho*" BPZ/Ag(I) complex. Hence, our calculations confirm that the observed SERS doublets are due to the coexistence of two different interactions of BPZ with the silver surface.

It is important to stress that the correlation between the SERS bands and the calculated wavenumbers has been performed by means of the vibrational assignment of bands in terms of Potential Energy Distribution (PED). For example, the SERS band at 1017 cm^{-1} is assigned to the calculated wavenumber at 1012 cm^{-1} of the "*meta*" conformer, which is described as in–plane ring bending. For the same conformer, however, there is another calculated mode at about the same position (*i.e.* the two modes are "accidentally degenerate") and another mode occurs at 1012 cm^{-1} for the "*ortho*" conformer. But these latter calculated vibrational modes, being described by PEDs as CH out–of–plane bending, cannot reasonably correspond to the strong SERS band at 1017 cm^{-1}.

4 CONCLUSIONS

B3LYP/LANL2DZ calculations of BPZ/Ag(I) surface complex models were performed in order to get a better insight into the adsorption behaviour of BPZ on the silver surface. From the comparison between the SERS data and the calculated wavenumbers, the occurrence of two different interactions of BPZ with the silver colloidal nanoparticles is confirmed. BPZ adsorbs with the silver surface through the nitrogen atom in *meta* or in *ortho* position and the doublets present in the SERS spectra are ascribed to the presence of both the conformers of BPZ/Ag(I) on the silver surface.

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