# Differentiated adsorption of thiobenzoic acid and thiobenzamide on silver nanoparticles determined by SERS spectroscopy

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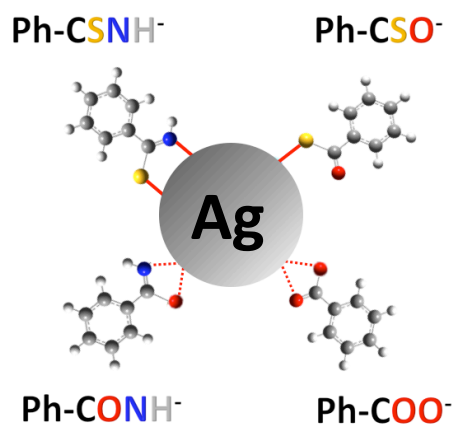
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ABSTRACT

Surface-enhanced Raman scattering of thiobenzoic acid and thiobenzamide have been recorded on three different silver colloids in order to find the chemical species responsible for the spectra and to detect differences in the adsorption with respect to their oxygen counterparts, benzoic acid and benzamide, respectively. Very significant and unexpected shifts of opposite sign between the Raman and SERS wavenumbers have been detected. By comparing the experimental and DFT calculated wavenumbers, it can be concluded that the acid is bonded to the metal as thiobenzoate through the sulfur atom with unidentate coordination. SERS spectra of thiobenzamide can be explained by assuming that it is adsorbed as azanion, like in the case of benzamide, linking to the metal through the sulfur and nitrogen atoms of the ionized thiocarboxamide group. In order to support these conclusions, B3LYP/LanL2DZ force field calculations for different complexes of silver cations with the thiobenzoate anion, the neutral thiobenzamide as well as its azanion have been carried out. Additionally, the 8a;ν_{ring} mode is the most enhanced band in the SERS of both adsorbates pointing to the participation of a metal-to-molecule resonant charge transfer mechanism.

1. Introduction

Nowadays, there is a general consensus on the main role of localized surface plasmon resonances (LSPR) in the enhancement mechanism of surface-enhanced Raman scattering (SERS). LSPR causes an enormous enhancement of the Raman signal from molecules near to or adsorbed on nanostructured surfaces of Cu, Au and, very especially, Ag [1-4]. Forty years after its discovery, the improvement of substrates and devices at the nanoscale have increased the applications of SERS in different fields, namely biochemistry and biosensing, catalysis or electrochemistry [5,6]. Consequently, SERS is one of the most powerful techniques to study adsorption processes at very low concentrations, even at molecular level, providing information on the adsorbed species, the functional groups interacting with the surface and the changes in the electronic structure of the adsorbate.

The relevant information comes from the comparative analysis of the relative intensities and wavenumbers of the Raman and the corresponding SERS spectra. However, the interpretation of a particular SERS record can be a challenge given that unusual chemical species with unknown Raman spectrum can be present at the interface. Another difficulty is the old controversy about the origin of the selective enhancement of particular SERS bands which is related to the presence of enhancement mechanisms of different nature and selection rules [2,3]. The very popular propensity rules derived from the so-called electromagnetic enhancement mechanism of SERS have been widely invoked and are based on the enhancement or weakening of specific Raman/SERS bands what would allow to deduce the orientation of the molecule with respect to the metal surface [7,8]. More complex selection rules are derived

from additional enhancement mechanisms related to the effect of the adsorption or the presence of resonance Raman processes (chemical enhancement mechanism) involving excited electronic states of the molecule (surface-enhanced resonant Raman Scattering, SERRS), metal-adsorbate photoinduced charge transfer (CT) processes (CT-SERS), or even other electronic resonances of the surface complex [9,10]. Although these chemical contributions are usually considered as secondary in SERS, they can dominate the relative intensities of the bands in a particular spectrum. Depending on the molecule, the metal and the experimental conditions, both mechanisms can operate simultaneously, making very difficult to recognize and to evaluate their relative contributions. However, the vibrational wavenumbers are not dependent on the SERS enhancement mechanisms and a very detailed information about the molecular adsorption can be obtained by comparing the Raman and SERS spectra [11]. This work is focussed on the analysis of the wavenumber shifts observed in the SERS of thiobenzoic acid and thiobenzamide upon adsorption on silver sols with the help of density functional theory (DFT) calculations. Additionally, the participation of photoinduced CT processes could be responsible for the specific enhancement of the characteristic $8a; \nu_{ring}$ band in the SERS of both adsorbates.

Thiocarboxylates are an interesting type of molecules having soft sulfur and hard oxygen donors able to bond with soft and hard metal centers, respectively [12]. Likewise, the sulfur and the nitrogen atoms of thiobenzamide can be coordinated to the surface. However, the chemistry of these molecules, especially thiobenzamide, has not been the subject of much attention in spite of having very interesting chemical, biological and pharmacological properties. For instance, the tautomerism of thiocarboxylic acids has been studied due to

the important role of –C(=S)O- and –C(=O)S- groups in the catalytic activities of enzymes such as cysteine or serine proteases [13]. On the other hand, thiobenzoic acid and its o-fluoro- and m-fluoro-derivatives are antimicrobial agents acting as fungicide against *Candida albicans* [14]. Thiobenzamides are used in turn as influenza inhibitors [15] and as drugs to control thyrotoxicosis [16], being well known by their hepatotoxicity [17], but a very important application is in corrosion inhibition of metals and alloys which are related to their adsorption properties [18].

The aims of this work is to study the effect of substituting oxygen by sulfur in the functional groups of benzene-like compounds on the adsorption process by comparing the SERS spectra of benzoic acid [19] and benzamide [20] with their respective sulfur derivatives, thiobenzoic and thiobenzamide. Although thiobenzoic acid has been used as a molecular probe for SERS substrates [21] and the Raman spectra of some thiobenzamide derivatives and complexes have been reported [22], this is the first SERS study of these two molecules which have a rich and complex structure with different tautomeric forms for protonated and deprotonated species (Fig. 1) able to bond to the metal surface in different ways.
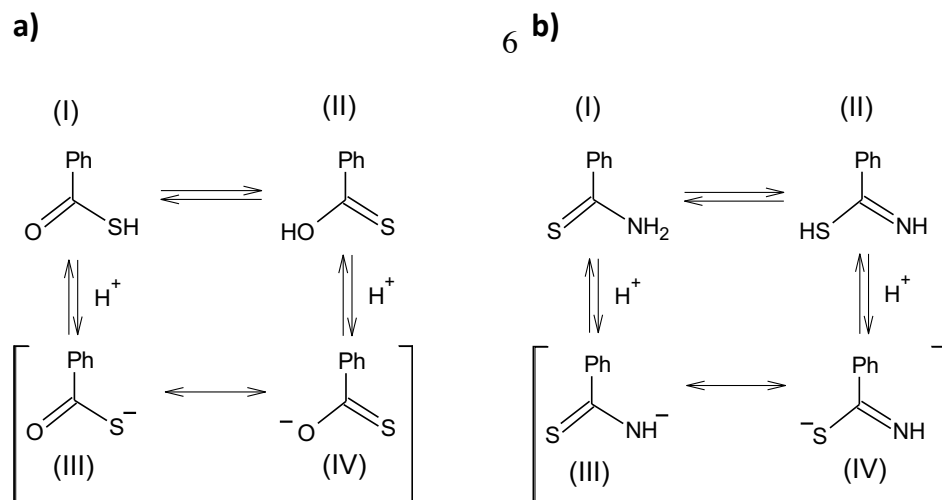
a)

b)

(I)   (II)   (I)   (II)

(III)   (IV)   (III)   (IV)

Fig. 1. Formation of: a) thiobenzoate (III,IV) and b) thiobenzamidate (III,IV) anions by deprotonation of the tautomeric forms of thiobenzoic acid (I,II) and thiobenzamide (I,II), respectively.

2. Methods

2.1 Experimental section

Reagents have been purchased from Sigma-Aldrich of the highest purity available. All the solutions were prepared by using Milli-Q quality water (resistivity over 18 MΩcm), and the final samples were prepared by adding the adsorbate to the colloid as an aqueous solution to obtain the desired concentration. pH was adjusted with a NaOH solution and was measured using standard paper strips.

Three different colloidal silver sols have been prepared which will be called Ag-BH, Ag-Hx and Ag-Ci henceforth:

a) Ag-BH has been obtained according to the method described by Creighton *et al*. [23], which basically consists of reducing one volume of 10^{-3} M AgNO₃

with three volumes of 2×10^{-3} NaBH$_4$ that has been previously cooled to a temperature between 0-5 ˚C.

b) Ag-Hx has been prepared by the method of Leopold and Lendl [24], by reducing AgNO$_3$ with hydroxylamine hydrochloride in a slightly alkaline medium. The hydroxylamine hydrochloride/silver nitrate relationship was chosen to reach 1.5×10^{-3} M/10^{-3} M ratio in the final reaction mixture.

c) Ag-Ci has been obtained following the method of Lee and Meisel [25] according to which 100 ml of an 1 mM AgNO$_3$ aqueous solution was heated to 90-100° C and then 2 ml of an 1% trisodium citrate solution was added. All the silver sols reported here have a final pH =7.

UV-VIS spectra of the respective silver sols can be seen in Fig. S1 and have been recorded in an Agilent 8453 spectrophotometer. Raman and SERS spectra were recorded by using different excitation lines from 488 up to 1064 nm. Figs. 2 and 4 show the spectra recorded under 514.5 nm excitation by using a Renishaw Invia micro-Raman spectrometer equipped with a charge-coupled device (CCD) camera at a resolution of 2 cm^{-1}. In the case of liquid samples a quartz cell of 1 cm pathlength was used while solids were directly recorded from the powder. SERS spectra at 532 and 633 nm were recorded by using a SENTERRA dispersive Raman Microscope (Bruker) and a RAM II FT-Raman module (Bruker) in the case of the 1064 nm exciting line. The acquisition time was 60 s in all the cases.

2.2 Theoretical calculations

All calculations have been carried out with the Gaussian 09 program package [26]. The optimized geometry and force field of all systems were calculated at B3LYP/LanL2DZ [27] level of theory. Becke's three parameter hybrid functional combined with the Lee-Yang-Parr correlation function (B3LYP) [28] was chosen amongst the DFT methods due to its good performance in molecular structure and force field calculations [29].

The effect of the adsorption on the wavenumber shifts has been analyzed by comparing the calculated wavenumbers of isolated and ionized species with their complexes with Ag^+. Rough metal surfaces have many different local structures at an atomic scale where a single molecule can be bonded. Such complex surfaces can be modelled by using large metal clusters in the calculations, but they show different geometries with several local sites of adsorption what forces to select, more or less arbitrarily, a particular structure and site for carrying out theoretical calculations. In this case, wavenumber shifts are very dependent on the charge of the metal atom directly bonded to the molecule while other atoms of the metal structure do not play any important role. This simple Ag^+–adsorbate model of the metal-adsorbate complex has shown to be useful in explaining the experimental shifts observed in the spectra of similar systems as well as in detecting the unexpected ionization of aromatic amides [20].

3. Results and discussion

3.1 Thiobenzoic acid (TBA)

Thioacids exist as tautomeric mixtures of both thiolic R-C(=O)SH and thionic R-C(=S)OH forms I and II in Fig. 1a, respectively. Previous studies have concluded that the corresponding equilibrium is strongly sensitive to the environment and the temperature. The majority form in solution is very depending on the nature of the solvent and can be modified in gas phase or in crystalline state [30,31]. Consequently, the SERS spectra of TBA have to be analysed by taking into account both tautomers if the neutral form is assumed to be the adsorbed species. Basic medium causes the deprotonation of either the -SH of the thiolic group (form I in Fig. 1a) or the -OH of the thionic species (form II), giving the two resonant structures (forms III and IV) of the thiobenzoate anion, respectively. The excess of delocalized negative charge in the anion would facilitate its bonding interaction with metal atoms of the surface as with carboxylic acids that are adsorbed as carboxylates on silver nanoparticles [19,32].

Figs. 2a and 2b show Raman spectra of pure liquid TBA and of 1 M aqueous solution at pH=14, respectively. Fig. 2c displays in turn the SERS spectrum of a 10^{-5} M solution in Ag-BH colloid at pH=7. SERS spectra of TBA at pH values up to 11 do not show any significant change, but the sol destabilizes when pH >11. The proposed assignment of the spectra of this molecule is summarized in Table S1 on the basis of previous SERS studies of benzoic acid and benzoate anion [19,32], the characteristic vibrational wavenumbers of thiocarboxylic and thiocarboxylate groups [33-35] as well as on force field results.
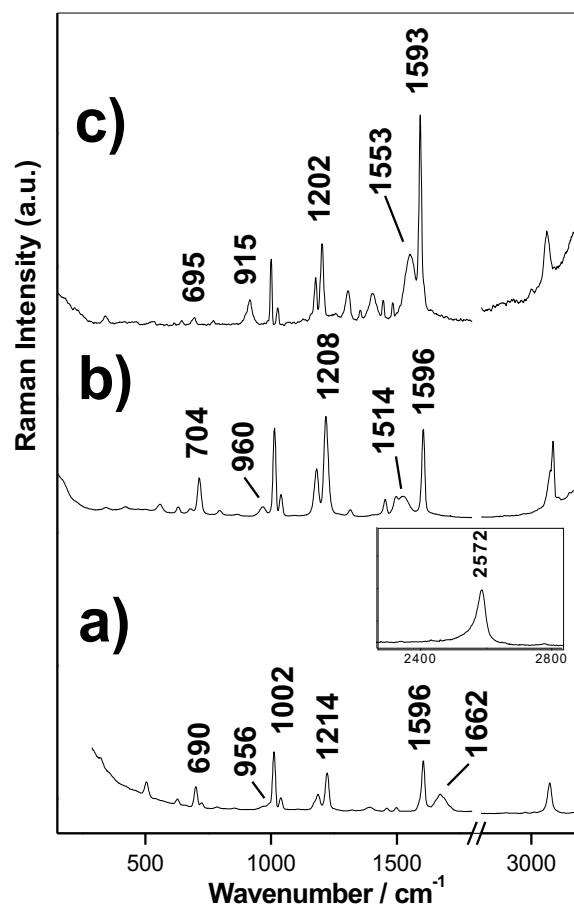
Fig. 2. Raman spectra of: a) liquid TBA, b) 1 M aqueous solution at pH=14, and c) SERS spectrum of a 10^{-5} M solution on Ag-BH silver colloid at pH=7 (514.5 nm excitation).

The Raman spectrum of pure liquid TBA (Fig. 2a) shows three very strong bands at 1002, 1214 and 1596 cm^{-1} assigned to 12;δ_{ring}, ν(CX) (ring-substituent stretching) and 8a;ν_{ring} vibrational modes, respectively. Medium intensity bands recorded at 1662 and 2572 cm^{-1} must be clearly assigned to ν(C=O) and ν(SH) stretching modes, respectively. The presence of these bands and the absence of ν(C=S) and ν(C-O) vibrations, whose expected wavenumbers would be around 900 and 1300 cm^{-1} respectively, point out that the spectrum of Fig. 1a is

originated by the thiolic form I of TBA (Fig. 1a). Other bands observed at 690 and 956 cm^{-1} correspond to vibrations 1;ν_{ring} and ν(C-S), respectively.

The ν(SH) fundamental is not observed in the Raman spectrum of deprotonated TBA$^-$ in aqueous solution at pH=14 (Fig. 2b). In turn, the ν(C=O) vibration is recorded at 1514 cm^{-1} and undergoes a very significant red-shift amounting to -148 cm^{-1} with respect to the Raman of the pure liquid (1662 cm^{-1}), whereas the ν(CS) band appears at 960 cm^{-1}, very close to its frequency in the spectrum of the pure liquid (956 cm^{-1}). This assignment is supported by the B3LYP/LanL2DZ calculated wavenumbers which amount to 1662/1500 cm^{-1} and 952/923 cm^{-1} for the ν(C=O) and ν(CS) vibrations of the acid/anion species, respectively (Fig. 3). Other two bands recorded at 1208 and 704 cm^{-1} are assigned to the ring-substituent ν(CX) vibration and to mode 1;ν_{ring}, which are only shifted -6 and +14 cm^{-1}, respectively.

SERS spectra of TBA at pH=7 obtained with the three different silver sols are very similar (Fig. S2) and, therefore, all the discussion will be referred to the intensities and wavenumbers of the SERS obtained using the Creighton's Ag-BH sol shown in Fig. 2c. SERS bands of TBA can be easily correlated with the Raman lines of the aqueous solution (Fig. 2b). There is no evidence of the appearance of the ν(SH) band indicating that thiobenzoate anion is the adsorbed species. It can also be observed the noticeable wavenumber shifts undergone by the SERS bands assigned to ν(C=O) and ν(CS) modes at 1553 and 915 cm^{-1}, respectively. Both of them are strong in SERS, but the most enhanced one is mode 8a;ν_{ring} whose band, recorded at 1593 cm^{-1}, dominates this spectrum.

System:	TBA neutral	TBA⁻ anion
Vibration:	1;ν_{ring} / ν(CS) / ν(C=O)	1;ν_{ring} / ν(CS) / ν(C=O)
Raman:	690 / 956 / 1662	704 / 960 / 1514
Calculated:	686 / 952 / 1662	698 / 923 / 1500

System:	Complex I	Complex II
Vibration:	1;ν_{ring} / ν(CS) / ν(C=O)	1;ν_{ring} / ν(CS) / ν(C=O)
SERS:	695 / 915 / 1553	695 / 915 / 1553
Calculated:	704 / 907 / 1435	694 / 922 / 1465

System:	Complex III	Complex IV
Vibration:	1;ν_{ring} / ν(CS) / ν(C=O)	1;ν_{ring} / ν(CS) / ν(C=O)
SERS:	695 / 915 / 1553	695 / 915 / 1553
Calculated:	710 / 936 / 1432	691 / 895 / 1584

Fig. 3. Structures of neutral TBA, TBA⁻ anion and Ag⁺-TBA⁻ complexes as well as experimental, Raman and SERS, and B3LYP/LanL2DZ calculated wavenumbers (cm⁻¹) of selected vibrations.

In our previous study on the SERS of benzoic acid (Ph-COOH) [20], the adsorption process has been correlated to the wavenumber shifts of two selected fundamentals when the deprotonation of the acid group takes place (Ph-COO⁻). These vibrations are the 1;ν_{ring} mode, strongly coupled with ν(CX) stretching and δ(COO) deformation coordinates, and the symmetric stretching of both CO bonds given that the ν_{as}(COO) antisymmetric mode is very weak in SERS. The most characteristic feature is the blue-shift of mode 1 when deprotonation occurs, from 795 to 844 cm⁻¹. The subsequent adsorption of benzoate anion on the silver surface (Ph-COO⁻/Ag⁺) causes smaller shifts of the wavenumbers of these modes with respect to free carboxylate. All these changes have been summarized in Table 1.

In the case of ionized TBA⁻, both C-S and C=O bonds remain uncoupled and this is why the behaviours of benzoic and thiobenzoic acids are different. It has already mentioned the noticeable red-shift of ν(C=O) stretching mode of TBA but, unlike the case of benzoic, ν(C-S) (-45 cm⁻¹) and ν(C=O) (+39 cm⁻¹) modes also shift upon adsorption, while vibration 1 does not. These results point to a different interaction of benzoic and thiobenzoic acids with the metal surface.

Table 1

Experimental Raman and SERS wavenumbers of selected bands of benzoic and thiobenzoic acids as well as the corresponding ionized benzoate and thiobenzoate species.

	Raman	Raman	SERS
System:	Ph-COOH	Ph-COO⁻	Ph-COO⁻/Ag⁺
Vibrational modes:	1;ν_{ring} / ν(C-O) / ν(C=O)	1;ν_{ring} / ν_s(COO)	1;ν_{ring} / ν_s(COO)
Wavenumber (cm⁻¹):	795 / 1290 / 1635	844 / 1394	845 / 1390
System:	Ph-COSH	Ph-COS⁻	Ph-COS⁻/Ag⁺
Vibrational modes:	1;ν_{ring} / ν(C-S) / ν(C=O)	1;ν_{ring} / ν(C-S) / ν(C=O)	1;ν_{ring} / ν(C-S) / ν(C=O)
Wavenumber (cm⁻¹):	690 / 956 / 1662	704 / 960 / 1514	695 / 915 / 1553

Different types of coordination between thiobenzoate anion and silver cations are shown in Fig. 3, namely (I) bridging bidentate, (II) chelating and (III and IV) unidentate ligands. A comparison between ν(C=O) and ν(CS) wavenumbers recorded in the SERS and in the Raman of the aqueous solution at pH=14 can help to clarify the structure of the metal-adsorbate complex. In the case of complex I, the wavenumbers of ν(C=O) and ν(CS) vibrations will be lowered with respect to the thiobenzoate anion. It should be expected that

these modes do not shift very much upon bidentate coordination (complex II). On the contrary, unidentate complex through the oxygen atom (complex III) must increase $\nu(CS)$ and reduce $\nu(C=O)$ wavenumbers while the opposite behaviour is expected if the adsorption takes place through the sulfur atom (complex IV). The SERS of Fig. 2c shows shifts of +39 and –45 cm^{-1} for $\nu(C=O)$ and $\nu(CS)$ bands, respectively, which are compatible with the Ag^{+}-TBA complex IV, i.e, unidentate coordination through the sulfur atom.

In order to confirm the structure of this surface complex, B3LYP/LanL2DZ calculations of the equilibrium geometries and the respective force fields of TBA monomer, TBA^{-} anion and the metal-TBA complexes shown in Fig. 3 have been carried out. The following discussion focuses on the wavenumber shifts undergone by 1; ν_{ring}, $\nu(CS)$ and $\nu(C=O)$ vibrational modes. The experimental Raman wavenumbers of TBA acid and TBA^{-} anion of these three modes are 690/956/1662 and 704/960/1514 cm^{-1}, respectively (Figs. 2a and 2b) correlating very well with the calculated values of 686/952/1662 and 698/923/1500 cm^{-1}, respectively. SERS wavenumbers of these vibrational modes are 695/915/1553 cm^{-1} and can be compared to the calculated ones for different Ag^{+}-TBA^{-} complexes depicted in Fig. 3. As a result, only the calculated wavenumbers of unidentate complex IV agree with the experimental results. The set of calculated shifts between TBA^{-} and Ag^{+}-TBA^{-} amounts to -7, -28 and +84 cm^{-1} for 1; ν_{ring}, $\nu(CS)$ and $\nu(C=O)$ modes, respectively, in agreement with the observed -9, -45 and +39 cm^{-1} in SERS, respectively.

The optimized geometries and the theoretical Raman spectra of complexes I, II, III and IV are shown in Fig. S3. It can be seen that the relative intensities of complex IV are very similar to those in the SERS spectrum of Fig. 2c. The C-S-Ag bond angle is *ca.* 120° in the case of complex IV (Fig. S3) and therefore,

the chelating interaction with the metal, which involves also the oxygen atom, must be discarded.

Concerning the intensities, it should be stressed the enhancements of the SERS bands assigned to ν(CS) and ν(C=O) fundamentals and recorded at 915 and 1553 cm^{-1}, respectively, that could be related to the proximity of the –OCS$^-$ group to the metal, but the strongest enhancement is shown by the 8a;ν_{ring} band 1593 cm^{-1} which could be due to the participation of a resonant charge transfer mechanism (SERS-CT) as will be discussed later.

3.2 Thiobenzamide (TBM)

The adsorption of thiobenzamide (TBM) on silver nanoparticles has specific characteristics that do not allow to record good SERS spectra with some of the silver sols. This is due to the very fast aggregation process after the addition of the adsorbate to the silver colloid, which destabilizes the final mixture within a few seconds and prevents the measurements. Fig. S4b shows the SERS recorded on Ag-Hx and the poor spectrum obtained with Ag-BH sol (Fig. S4a) which gives similar results to than the Ag-Ci colloid. This means that the adsorption of thioamide is much stronger than the corresponding acid, what is a surprising result given that the carboxylate anions should be bonded to the metal surface more strongly than neutral species such as amides or thioamides derivatives. Figs. 4a and 4b show the Raman spectrum of solid TBM and the SERS spectrum of a 10^{-5} M TBM solution on Ag-Hx colloid at pH=7, respectively. The very low solubility of TBM in water, even under very basic conditions, prevents recording the Raman spectrum of the aqueous solution. The vibrational assignment of the Raman and SERS spectra of TBM are summarized in Table S2 on the basis of previous studies of this molecule

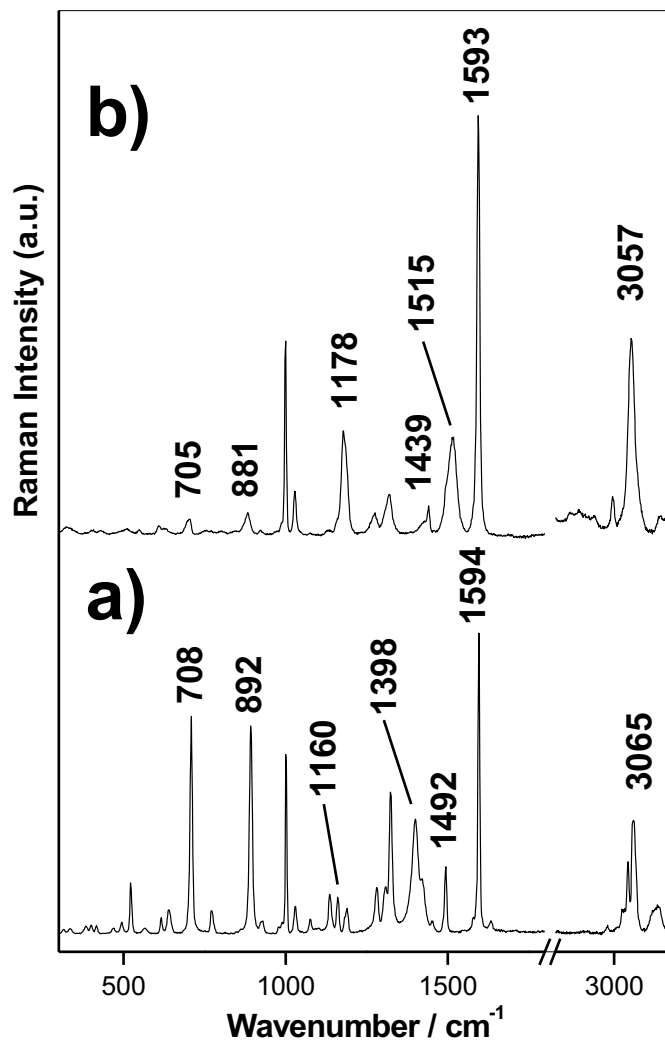[36], the characteristic wavenumbers of the thiocarboxamide group [35] and the force field calculations.

Fig. 4. Raman spectra of: a) solid TBM and b) SERS spectrum of a 10^{-5} M solution on Ag-Hx silver colloid at pH=7 (514.5 nm excitation).

The very strong band recorded at 1594 cm^{-1} in the Raman spectrum of solid TBM (Fig. 4a) is assigned to the 8a;ν_{ring} vibration. Two strong bands recorded

at 892 and 708 cm^{-1} correspond to Thioamide I (mainly ν(C=S)) and 1;ν_{ring} fundamentals, respectively, while the medium intensity band at 1398 cm^{-1} is assigned to Thioamide III, (mainly ν(CN)). It is noticeable the relative enhancement undergone in the SERS spectrum of TBM (Fig. 4b) of the 8a;ν_{ring} and ν(CX) bands at 1593 and 1178 cm^{-1}, respectively. On the contrary, the bands assigned to vibrations 1;ν_{ring} and ν(C=S) are recorded very weak at 705 and 881 cm^{-1}, respectively. This assignment would agree with previous studies of complexes of TBM with gold(I), nickel(II) and palladium(II), where ν(CN) and ν(C=S) bands are recorded in the 1400-1450 cm^{-1} and 850-890 cm^{-1} ranges, respectively [37,38].

The 1515 cm^{-1} SERS band is not trivial to assign. It is not enhanced in the SERS or benzamide or salycilamide [20] and could correspond to mode 19a;ν_{ring} recorded at 1492 cm^{-1} in the Raman spectrum of solid, but this ring stretching vibration is not usually enhanced in the SERS of benzenelike derivatives. The noticeably enhancement and broadness of the 1515 cm^{-1} band aim to be assigned as ν(CN) in agreement with adsorption studies of thioacetamide on silver electrodes where this vibration is recorded at 1497 cm^{-1} [39]. Theoretical calculations support this assignment.

The main and unexpected conclusion from our previous studies on the SERS of benzamide, salycilamide [20], pyrazinamide [40] and pyridinamides [41] is that these compounds deprotonate when are adsorbed on silver sols. The bands of these amides corresponding to 1;ν_{ring}, Amide I (mainly ν(C=O)) and Amide III (mainly ν(CN)) are shifted *ca.* +50, -40 and +10 cm^{-1} in SERS with respect to the normal Raman spectrum, respectively, due to the interaction of both O and N atoms of the ionized carboxamide group with the metal surface [20,41]. In the case of TBM the behaviour is quite different: mode 1;ν_{ring}

remains almost unshifted in SERS while Thioamide I (ν(C=S)) and Thioamide III (ν(CN)) bands are shifted but in very different amounts and opposite directions, -11 and +117 cm^{-1}, respectively. Therefore, the replacement of the oxygen of amide group by a sulfur atom produces significant differences in the behaviour of the SERS spectra.

B3LYP/LanL2DZ calculations of neutral TBM predict the wavenumbers 708, 883 and 1393 cm^{-1} for 1;ν_{ring}, ν(C=S) and ν(CN) fundamentals, respectively, in agreement with the Raman spectrum of solid TBM where they are observed at 708, 892 and 1398 cm^{-1}, respectively. Thioamides are neutral species scarcely soluble in water and their respective anions cannot be obtained even under extreme basic conditions. The hypothetical formation of the thiobenzamidate anion TBM$^-$ can be originated by the deprotonation of either the thionic (I) or thiolic (II) tautomers, producing two anionic forms (III and IV, respectively), which can be considered as resonant structures of the azanion TBM$^-$ (Fig. 1b). The excess of negative charge localized in the nitrogen and sulfur atoms of this anionic species would facilitate the bonding with the metal. The B3LYP/LanL2DZ calculated wavenumbers for the three mentioned fundamentals of TBM$^-$ anion are 687, 863 and 1493 cm^{-1}, respectively (Fig. 5), being noticeable the blue-shift undergone by ν(CN) with respect to neutral TBM. This result supports the possibility that the broad SERS band at 1515 cm^{-1} is assigned to the ν(CN) vibration instead of mode 19a.

System:	TBM neutral	TBM⁻ anion	
Vibration:	$1;\nu_{ring}$ / $\nu(CS)$ / $\nu(CN)$	$1;\nu_{ring}$ / $\nu(CS)$ / $\nu(CN)$	
Raman:	708 / 892 / 1398		
Calculated:	708 / 883 / 1393	687 / 863 / 1493	

System:	Complex I	Complex VII	Complex VIII
Vibration:	$1;\nu_{ring}$ / $\nu(CS)$ / $\nu(CN)$	$1;\nu_{ring}$ / $\nu(CS)$ / $\nu(CN)$	$1;\nu_{ring}$ / $\nu(CS)$ / $\nu(CN)$
SERS:	705 / 881 / 1515	705 / 881 / 1515	705 / 881 / 1515
Calculated:	687 / 851 / 1450	688 / 894 / 1492	701 / 892 / 1506

Fig. 5. Structures of neutral TBM monomer, TBM⁻ anion, Ag⁺-TBM and Ag⁺-TBM⁻ complexes as well as experimental, Raman and SERS, and B3LYP/LanL2DZ calculated wavenumbers of selected vibrations (cm⁻¹).

DFT calculations of different metal-molecule complexes shown in Fig. S5 have been carried out in order to confirm this assignment as well as to identify the type of coordination established between thiobenzamide and the silver nanoparticles. Neutral molecule is acting in the TBM-Ag⁺ complexes (Fig. S5a) as unidentate ligand bonded either through the sulfur (complex I) or the nitrogen atoms (complex II), as chelating ligand (complex III), and as bridging bidentate ligand (complex IV). Furthermore, theoretical calculations have also been done for similar complexes with the TBM⁻ azanion by assuming that the thiocarboxamide group deprotonates upon adsorption. These four models are labelled as V, VI, VII and VIII in Fig. S5b. All the geometries have been optimized and the corresponding normal modes have been calculated at B3LYP/LanL2DZ level, focussing the discussion on the wavenumbers of the characteristic $1;\nu_{ring}$, $\nu(C=S)$ and $\nu(CN)$ fundamentals.

Optimization of the geometries of complex II and III (Fig. S5a) leads to the same final structure of complex I. A similar behaviour is observed in complexes V and VI converging, in these cases, towards the structure of complex VII. While all of the discussed systems have a planar structure, the optimized geometry of complex IV looks like complex I but with a second silver atom located out of the ring plane and close to a CH bond in ortho position (see Fig. S6). Therefore, the eight models initially considered are reduced to the three complexes I, VII and VIII shown in Fig. 5. This Figure summarizes also the respective experimental Raman and SERS wavenumbers as well as the calculated values for vibrations 1;ν_{ring}, $\nu(C=S)$ and $\nu(CN)$ of TBM neutral, TBM$^-$ anion and these complexes. In spite of the simple metal-adsorbate models assumed to simulate the real systems, a quite good agreement between calculated and experimental wavenumber shifts is obtained in the case of complexes VII and VIII. Only these two forms are able to account for the experimental shifts observed for these three fundamentals, -3, -11 and +117 cm^{-1}, respectively. The calculated values are –20, -11 and +99 cm^{-1} for complex VII and -7, +9 and +113 cm^{-1} for complex VIII, respectively. Fig. S6 shows the optimized geometries of complexes I, IV, VII and VIII and the corresponding calculated Raman spectra. It is remarkable the agreement between the calculated spectrum for complex VIII and the experimental SERS.

Summarizing, the analysis of the SERS wavenumbers points out that TBM is adsorbed on silver nanoparticles as azanion and links to the metal through the nitrogen and sulfur atoms of the deprotonated thiocarboxamide group, acting either as bridging bidentate ligand (complex VIII) or as chelating ligand (complex VII). Electron rich donors, such as carboxylate anions, are very good ligands and have strong affinity for silver or gold surfaces, while neutral species, like amides, should be less likely to be adsorbed. The much faster

precipitation of thiobenzamide-sol than thiobenzoic-sol samples is evidence of the deprotonation of the amide group. The corresponding amidate anion is strongly adsorbed and causes the fast flocculation of the colloidal solution because of the external non-polar part of the molecule reduces the repulsion between surface charges of the covered nanoparticles. Colloid aggregation caused by adsorbed molecules is a very well known phenomenon in SERS [2,3] and a standard topic in colloidal science [42,43].

3.3 Charge transfer mechanism in the SERS of TBA

Besides the shifts between the Raman and SERS wavenumbers, it is interesting to analyse changes in the relative intensities of the bands of both types of spectra given that the selective intensification of particular SERS lines can be related to the presence of different enhancement mechanisms [2,3]. This is a controversial subject in SERS due to the difficulty of recognizing the presence of physical/plasmonic [7,8,44] and/or chemical [8,45] contributions to the overall enhancement. The most important chemical contribution is due to photoinduced metal-molecule charge transfer resonances, which is similar to a resonance Raman process occurring when the energy of the laser photon matches that of an excited CT state of the metal-molecule surface complex [9].

We have shown in previous studies of six-membered aromatic molecules [46,47] that the main feature of a SERS spectrum where resonant metal-to-molecule CT processes are present (SERS-CT) is the strong and selective enhancement of the band corresponding to the $8a; \nu_{ring}$ mode, which is recorded at characteristic wavenumbers of about 1600 cm^{-1}. Consequently, we have proposed a simple *propensity rule* to detect the participation of the CT enhancement mechanism in a particular spectrum of benzene-like molecules by

checking the selective enhancement of this normal mode. The greater or lesser contribution of the SERS-CT mechanism in a spectrum depends on the nature of the adsorbate and the metal as well as on the experimental conditions [46,47], especially the electric potential of the interface and the energy of the laser excitation [9,47] which determine the resonant condition. For this reason, the presence of resonant processes can be detected by studying the dependence of the relative intensities on the energy of the laser photon [48].

SERS spectra of TBA and TBM are characterized by the strong selective enhancement of the $8a;\nu_{ring}$ band (Figs. 2 and 4). This vibration is recorded at 1593 cm^{-1} in both cases, being particularly strong in the SERS of the acid. This result points to the participation of the SERS-CT enhancement mechanism in the spectra of both adsorbates. A series of SERS spectra excited at several wavelengths have been recorded in order to observe the effect of the excitation energy on the relative intensities of the bands. This study focuses on the SERS of TBA in Ag-Ci colloids given the very fast flocculation of TBM samples. TBA/Ag-Ci samples are moderately stables and with a large distribution of aggregates of different sizes and shapes allowing to use a wide range of excitation energies which are red-shifted with respect to the broad plasmons resonances (Fig. 6b) [49].
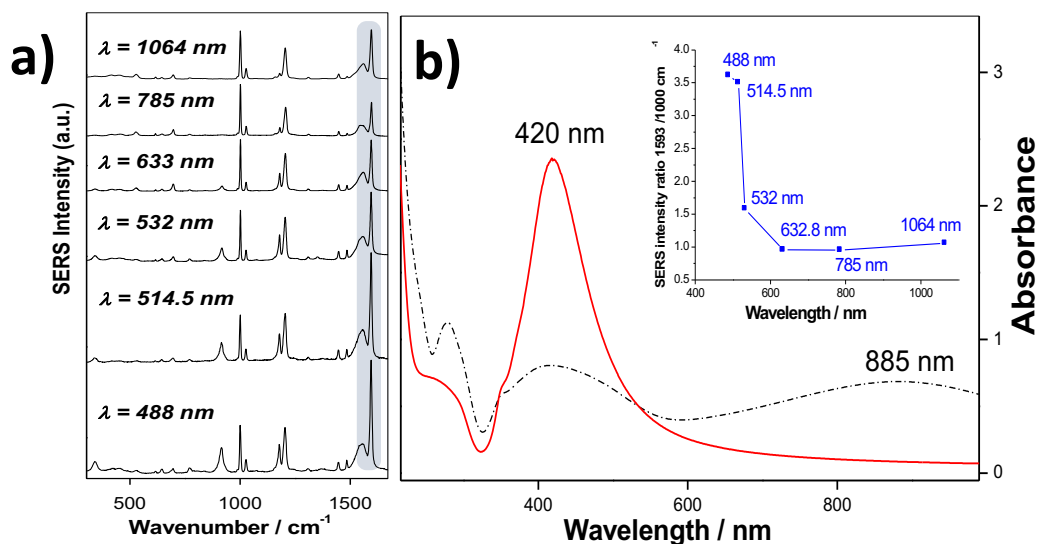
Fig. 6. a) SERS spectra of 10^{-5} M solutions of TBA on Ag-Ci sols with different exciting wavelengths. b) UV-vis spectra of Ag-Ci colloid (solid line) and of aggregated solutions of 10^{-5} M TBA on Ag-Ci sols (dotted line). Inset in Fig. 6b shows the dependence on the exciting wavelength of the ratio between the SERS intensities of the 1593 and 1000 cm^{-1} bands.

Fig. 6a shows the SERS spectra of 10^{-5} M solutions of TBA on Ag-Ci sols recorded with different exciting lines, from 488 nm to 1064 nm. It can be seen that the band of mode 8a becomes stronger as the laser lines are more energetic. This implies the presence of a resonant Raman process and rules out the adsorption as the cause of its selective enhancement. Strong adsorption can modify the electronic structure of these adsorbates in the ground electronic state and, therefore, could modify the relative intensities but this effect should not be sensitive to the excitation energy.

The inset in Fig. 6b shows the ratio between the intensities of the 1593 and 1000 cm^{-1} SERS bands of modes 8a and 12;δ_{ring}, which has been taken as an internal standard. The ratio ranges between 1, with the 1064 nm line, up to 3.8, when the 488 nm line is used, which should be close to the maximum of the CT electronic transition given that the relative intensities of this last spectrum are very similar to that recorded at 514.5 nm. This implies that the energy of the excited metal-to-molecule charge transfer state should be of the order of these two more energetic laser lines, ca. 2.4-2.5 eV.

Finally, it should be stressed that the assignment of the vibrations of these two molecules on the basis of the Wilson´s nomenclature [50] and of simple internal coordinates for the functional group can only be considered as rough labels for the normal modes where several internal motions can be coupled in a complex way. Figs. S7 and S8 summarize the calculated wavenumbers and the corresponding atomic displacements of the selected vibrations of both systems.

4. Conclusions

The analysis of the Raman and SERS spectra with the help of DFT calculations has allowed to conclude that thiobenzoic acid is adsorbed on colloidal silver nanoparticles through the sulfur atom (monodentate) of its anionic species. Thiobenzamide is also adsorbed deprotonated on the silver surface just as others aromatic amides do [20,41]. This can be the cause of the very fast flocculation of the colloids when thiobenzamide is added. The corresponding azanion links to the metal through the sulfur and nitrogen atoms of the ionized thiocarboxamide group (bridging bidentate). The adsorption of the corresponding oxygen derivatives, benzoic [19] and benzamide [20], is quite different. They are also deprotonated upon adsorption, but both CO/CO or CO/CN bonds are involved in the bonding to the silver surface, giving bidentate coordination. This differentiated behaviour is due to the strong affinity of sulfur for the surface given that a single silver atom can only bind to a sulfur in monodentate or bridging bidentate complexes, respectively.

The substitution of light oxygen by a heavier sulfur modifies the characteristic vibrations of the function group as well as the coupling between the internal coordinates of the substituent and the ring-stretching modes. Vibration 1 undergoes a significant blue-shift when benzoic or benzamide are

losing the proton while its wavenumber remains almost unchanged in the corresponding thio-derivatives. ν(C=O) and ν(CS) vibrations of thiobenzoate shift +39 and –45 cm^{-1}, respectively, while ν(CN) and ν(C=S) modes are shifted +117 and –11 cm^{-1} in the spectra of thioamide, respectively.

Finally, the strong relative enhancement of the characteristic band of the 8a;ν_{ring} fundamental observed in the SERS of both molecules confirms the participation of resonant photoinduced CT processes between the metal and the adsorbates.

CRediT authorship contribution statement

María Rosa López-Ramírez: Conceptualization, Investigation, Visualization, Writing - original draft. **Daniel Aranda:** Software, Writing - review & editing. **Isabel López-Tocón:** Supervision, Investigation. **Juan Soto:** Investigation, Methodology, Software. **José Luis Castro:** Conceptualization, Investigation, Resources, Writing - original draft, Writing - review & editing. **Juan Carlos Otero:** Investigation, Writing - original draft, Writing - review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at

References

[1] K. A. Willets, R. P. Van Duyne, Localized surface plasmon resonance spectroscopy and sensing, Annu. Rev. Phys. Chem. 58 (2007) 267-297. DOI: https://doi.org/10.1146/annurev.physchem.58.032806.104607

[2] M. Moskovits, Surface-enhanced spectroscopy, Rev. Mod. Phys. 57 (1985) 783-826. DOI: https://doi.org/10.1103/RevModPhys.57.783

[3] R. Aroca, Surface-enhanced vibrational spectroscopy, John Wiley & Sons, Chichester, 2006. https://doi.org/10.1002/9780470035641.ch7

[4] E. C. Le Ru, P. G. Etchegoin, Principles of surface enhanced Raman spectroscopy and related plasmonic effects, Elsevier, Amsterdam, 2008. https://doi.org/10.1016/B978-0-444-52779-0.X0001-3

[5] A. El-Ansary, L. M. Faddah, Nanoparticles as biochemical sensors, Nanotechnol. Sci. Appl. 3 (2010) 65-76. DOI: https://doi.org/10.2147/NSA.S8199

[6] W. F. Paxton, S. L. Kleinman, A. N. Basuray, J. F. Stoddart, R. P. Van Duyne, Surface-enhanced Raman spectroelectrochemistry of TTF-modified self-assembled monolayers, J. Phys. Chem. Lett. 2 (2011) 1145-1149. DOI: https://doi.org/10.1021/jz200523q

[7] M. Moskovits, D. P. DiLella, K. J. Mainard, Surface Raman spectroscopy of a number of cyclic aromatic molecules adsorbed on silver: selection rules and molecular reorientation, Langmuir 4 (1988) 67-76. DOI: https://doi.org/10.1021/la00079a012

[8] J. A. Creighton, The selection rules for surface-enhanced Raman spectroscopy. In: Advances in Spectroscopy: Spectroscopy of surfaces, Eds: R. J. H. Clark, R. E. Hester, John Wiley & Sons, Chichester, 1988, 37-89. ISSN: 0892-2888.

[9] F. Avila, D. J. Fernandez, J. F. Arenas, J. C. Otero, J. Soto, Modelling the effect of the electrode potential on the metal-adsorbate surface states: relevant states in the charge transfer mechanism of SERS, Chem. Commun. 47 (2011) 4210-4212. DOI: https://doi.org/10.1039/C0CC05313A

[10] A. Otto, I. Mrozek, H. Grabhorn, W. J. Akemann, Surface-enhanced Raman scattering, J. Phys.: Condens. Matter 4 (1992) 1143-1212. DOI: https://doi.org/10.1088/0953-8984/4/5/001

[11] J. Soto, D. J. Fernandez, S. P. Centeno, I. Lopez Tocon, J. C. Otero, Surface orientation of pyrazine adsorbed on silver from the surface-enhanced Raman

scattering recorded at different electrode potentials, Langmuir 18 (2002) 3100-3104. DOI: https://doi.org/10.1021/la010489p

[12] R. G. Pearson, Hard and soft acid and bases, J. Am. Chem. Soc. 85 (1963) 3533-3543. DOI: https://doi.org/10.1021/ja00905a001

[13] P. Carey, Biochemical Applications of Raman and Resonance Raman Spectroscopy; Academic Press: London, 1982. ISBN: 9780121596507.

[14] G. R. Gale, H. H. McLain, Effect of thiobenzoate on cytology of Candida albicans, J. Gen. Microbiol. 36 (1964) 297-301. DOI: https://doi.org/10.1099/00221287-36-2-297

[15] K. L. Yu, A. F. Torri, G. Luo, C. Cianci, K. Grant-Young, S. Danetz, L. Tiley, M. Krystal, N. A. Meanwell, Structure-activity relationships for a series of thiobenzamide influenza fusion inhibitors derived from 1, 3, 3-Trimetryl-5-hydroxy-cyclohexylmethylamine, Bioorg. Med. Chem. Lett. 12 (2002) 3379-3380. DOI: https://doi.org/10.1016/S0960-894X(02)00761-8

[16] D. S. Cooper, Hyperthyroidism, Lancet, 362 (2003) 459-468. https://doi.org/10.1016/S0140-6736(03)14073-1

[17] T. Ji, K. Ikehata, Y. M. Koen, S. W. Esch, T. D. Williams, R. P. Hanzlik, Covalent modification of microsomal lipids by thiobenzamide metabolites in vivo, Chem. Res. Toxicol. 20 (2007) 701-708. DOI: https://doi.org/10.1021/tx600362h

[18] V. Pandarinathan, K. Lepkova, S. I. Bailey, R. Gubner, Inhibition of under-deposit corrosion of carbon steel by thiobenzamide, J. Electrochem. Soc. 160 (2013) C432-C440. DOI: https://doi.org/10.1149%2F2.078309jes

[19] M. R. Lopez-Ramirez, C. Ruano, J. L. Castro, J. F. Arenas, J. Soto, J. C. Otero, Surface-enhanced Raman scattering of benzoate anion adsorbed on silver nanoclusters: evidence of the transient formation of the radical dianion, J. Phys.

Chem. C 114 (2010) 7666–7672 and references therein. DOI: https://doi.org/10.1021/jp911865w

[20] J. L. Castro, M. R. Lopez-Ramirez, J. F. Arenas, J. Soto, J. C. Otero, Evidence of deprotonation of aromatic acids and amides adsorbed on silver colloids by surface-enhanced Raman scattering, Langmuir 28 (2012) 8926-8932. DOI: https://doi.org/10.1021/la204702w

[21] W. Weber, A. Feis, C. Gellini, R. Pilot, P. R. Salvi, R. Signorini, Far- and near-field properties of gold nanoshells studied by photoacoustic and surface-enhanced Raman spectroscopies, Phys. Chem. Chem. Phys. 17 (2015) 21190-21197. DOI: https://doi.org/10.1039/C4CP05054A

[22] I. Rigane, S. Walha, A. Ben Salah, Hydrogen bonding in thiobenzamide synthon and its Cadmium complex: Crystal structure and Hirshfeld analysis, J. Chem. Sci. 128 (2016) 1395-1404. DOI: https://doi.org/10.1007/s12039-016-1133-x

[23] J. A. Creighton, C. G. Blatchford, M. G. Albrecht, Plasma resonance enhancement of Raman scattering by pyridine adsorbed on silver or gold sol particles of size comparable to the excitation wavelength, J. Chem. Soc., Faraday Trans. II 75 (1979) 790-798. DOI: https://doi.org/10.1039/F29797500790

[24] N. Leopold, B. Lendl, A new method for fast preparation of highly surface-enhanced Raman scattering (SERS) active silver colloids at room temperature by reduction of silver nitrate with hydroxylamine hydrochloride, J. Phys. Chem. B 107 (2003) 5723-5727. DOI: https://doi.org/10.1021/jp027460u

[25] P. C. Lee, D. J. Meisel, Adsorption and surface-enhanced Raman of dyes on silver and gold sols, J. Phys. Chem. 86 (1982) 3391-3395. DOI: https://doi.org/10.1021/j100214a025

[26] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A: Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision A.1; Gaussian, Inc.: Wallingford CT, 2009.

[27] P. J. Hay, W. Wadt, Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg, J. Chem. Phys. 82 (1985) 270-283. DOI: https://doi.org/10.1063/1.448799

[28] C. Lee, W. Yang, R. G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, Phys. Rev. B 36 (1988) 785-789. DOI: https://doi.org/10.1103/PhysRevB.37.785

[29] C. W. Bauschlicher Jr., A comparison of the accuracy of different functionals, Chem. Phys. Lett. 246 (1995) 40-44. DOI: https://doi.org/10.1016/0009-2614(95)01089-R

[30] J. S. Kwiatkowski, T. J. Zielinski, R. Rein, Quantum-mechanical prediction of tautomeric equilibria, Adv. Quantum Chem. 18 (1986) 85-130 and references cited therein. https://doi.org/10.1016/S0065-3276(08)60048-9

[31] D. Delaere, G. Raspoet, M. T. Nguyen, Thiol-thione tautomerism in thioformic Acid: Importance of specific solvent interactions, J. Phys. Chem. A 103 (1999) 171-177. DOI: https://doi.org/10.1021/jp983298c

[32] Y. J. Kwon, D. H. Son, S. J. Ahn, M. S. Kim, A. Kim, Vibrational spectroscopic investigation of benzoic acid adsorbed on silver, J. Phys. Chem. 98 (1994) 8481-8487. DOI: https://doi.org/10.1021/j100085a030

[33] R. A. Nyquist, W. J. Potts, Characteristic infrared absorption frequencies of thiol esters and related compounds, Spectrochim. Acta 7 (1959) 514-538. DOI: https://doi.org/10.1016/S0371-1951(59)80348-9

[34] V. V. Savant, J. Gopalakrishnan, C. C. Patel, Metal monothiobenzoates, Inorg. Chem. 9 (1970) 748-751. DOI: https://doi.org/10.1021/ic50086a011

[35] N. P. G. Roeges, A Guide to the complete interpretation of infrared spectra of organic structures. John Wiley & Sons, Chichester, 1994. ISBN: 978-0-471-93998-6.

[36] A. J. Aarts, H. O. Desseyn, B. J. Van der Veken, M. A. Herman, Vibrational analysis of thiobenzamide, N-methylthiobenzamide and N,N-dimethylthiobenzamide, Can. J. Spectrosc. 24 (1979) 29-34. ISSN. 0045-5105.

[37] A. J. Aarts, H. O. Desseyn, M. A. Herman, Complexes of nickel(II) and palladium(II) with thiobenzamide, Transition Met. Chem. 4 (1979) 46-48. DOI: https://doi.org/10.1007/BF00941017

[38] A. J. Aarts, H. O. Desseyn, M. A. Herman, Gold(I) complexes of thioamides, Transition Met. Chem. 5 (1980) 10-14. DOI: https://doi.org/10.1007/BF01396857

[39] B. H. Loo, Y. G. Lee, Surface-enhanced Raman spectroscopy study of the adsorption of thioacetamide on copper and silver electrodes, Chem. Phys Letters 112 (1984) 580-584. DOI: https://doi.org/10.1016/0009-2614(84)85783-8

[40] J. F. Arenas, J. L. Castro, J. C. Otero, J. I. Marcos, Surface-enhanced Raman spectra of pyrazinecarboxamide and pyrazinecarbonitrile on silver sols, J. Raman Spectrosc. 23 (1992) 249-252. DOI: https://doi.org/10.1002/jrs.1250230503

[41] J. L. Castro, J. F. Arenas, M. R. Lopez-Ramirez, J. Soto, J. C. Otero, Surface-enhanced Raman scattering of picolinamide, nicotinamide and isonicotinamide: Unusual carboxamide deprotonation under adsorption on silver nanoparticles, J. Colloid Interf. Sci. 396 (2013) 95-100. DOI: https://doi.org/10.1016/j.jcis.2013.01.050

[42] M. Moskovits, B. Vlckovà, Adsorbate-Induced Silver Nanoparticle Aggregation Kinetics, J. Phys. Chem. B 109 (2005) 14755-14758. DOI: https://doi.org/10.1021/jp051177o

[43] A. Henglein, Physicochemical Properties of Small Metal Particles in Solution: "Microelectrode" Reactions, Chemisorption, Composite Metal Particles, and the Atom-to-Metal Transition, J. Phys. Chem. 97 (1993) 5457-5471. https://doi.org/10.1021/j100123a004

[44] G. C. Schatz, R. P. Van Duyne, Electromagnetic Mechanism of Surface-Enhanced Spectroscopy. In: Handbook of Vibrational Spectroscopy, Eds: J. M. Chalmers and P. R. Griffiths, John Wiley & Sons, Chichester, 2006. https://doi.org/10.1002/0470027320

[45] A. Otto, The 'chemical' (electronic) contribution to surface-enhanced Raman scattering, J. Raman Spectrosc. 36 (2005) 497-509. https://doi.org/10.1002/jrs.1355

[46] F. Avila, C. Ruano, I. Lopez-Tocon, J. F. Arenas, J. Soto, J. C. Otero, How the electrode potential controls the selection rules of the charge transfer mechanism of SERS, Chem. Commun. 47 (2011) 4213-4215. DOI: https://doi.org/10.1039/C0CC05314G

[47] M. R. Lopez-Ramirez, J. V. Garcia-Ramos, J. C. Otero, J. L. Castro, S. Sanchez-Cortes, Tuning charge-transfer processes in the surface-enhanced Raman scattering of 1-α-phenylglycine adsorbed on silver nanostructures, Chem. Phys. Lett. 446 (2007) 380–384. https://doi.org/10.1016/j.cplett.2007.08.069

[48] K. Szlachetko, P. Piotrowski, K. Sadecka, P. Osewski, D. Kasprowicz, D. A. Pawlak, Selective surface-enhanced Raman scattering in a bulk nanoplasmonic Bi_2O_3-Ag eutectic composite, Nanophotonics 9 (2020) 4307–4314. https://doi.org/10.1515/nanoph-2020-0281

[49] R. A. Álvarez-Puebla, Effects of the Excitation Wavelength on the SERS spectrum, J. Phys. Chem. Lett. 3 (2012) 857-866. DOI: https://doi.org/10.1021/jz201625j

[50] G. Varsányi, Vibrational Spectra of Benzene Derivates, Academic Press Budapest, 1969. https://doi.org/10.1016/B978-0-12-714950-9.X5001-7