Adsorption of Mercaptoacetic Acid on a Colloidal Silver Surface as Investigated by Raman Spectroscopy

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Abstract: The vibration $\nu$(SH) has never been observed in the surface-enhanced Raman scattering of mercaptoacetic acid recorded in a wide range of pH. This behavior enables us to deduce that the $\sim$SH group is deprotonated and links to the metal forming an Ag–S bond as 1-alkanethiols do. On the contrary, the carboxylic or carboxylate groups do not link to the metal and the carboxylic group is preserved even at pH values under which it should be deprotonated. This fact enables the stabilization of the adsorbed monolayer by removing the electrostatic repulsions between $\sim$COO$^-$ groups and by the formation instead of hydrogen bonds between carboxylic groups. Only under rather basic conditions (pH $> 8$) does the carboxylic groups dissociate, but the $\nu$(OCO) band is neither enhanced nor shifted toward low frequencies.

Keywords: surface-enhanced Raman scattering; Raman; mercaptoacetic acid; thioglycolic acid

INTRODUCTION

In this work, the surface-enhanced Raman scattering (SERS) spectra of mercaptoacetic acid (MAA) adsorbed on colloidal silver surfaces was studied. MAA is an interesting compound from a biological point of view given that it has been used to synthesize some antiviral drugs$^1$ and it is shown to be a selective inhibitor of fatty acid oxidation by decreasing the plasmatic concentration of $\beta$-hydroxybutyrate and free fatty acids$^2$ and, therefore, increasing gluconeogenesis and glucemia levels.

The study of SERS spectra of mercaptoacids adsorbed on silver sols is interesting because they are bifunctional compounds able to interact with the metal through either any of the functional groups or both of them simultaneously. SERS techniques have allowed us to study vibrational spectra of several organic thiols adsorbed on silver surfaces, for instance, aromatic compounds like benzenethiol,$^3$ 2-mercaptopyrindine,$^4$ 2-mercaptopurinimidine,$^5$ and 4-mercaptoimidazol$^5$ as well as alkanethiols like 1-propanethiol,$^6$ 1-butethiol,$^7$ 2-butethiol,$^8$ and higher 1-alkanethiols.$^9,10$ In all cases, it is found that thiols adsorb on the metal surface via their sulfur atoms, after losing thiol protons. On the other hand, carboxylic acids are known to adsorb on metal surfaces as carboxylates.$^{11,12}$ The aim of this work has been to determine which functional groups are concerned in the adsorption and which ionic species is responsible for the observed spectra. This will allow us to determine whether the behavior observed in
colloids agrees with that observed on metal electrodes. The adsorbed species may be the minority in aqueous solution and may be impossible to study by spectroscopic techniques that are different from SERS. However, they can play an important role in some biological processes. Our results allow us to establish that the –SH group reacts with the metal to yield a stable sulfur-silver bond, while the carboxylic or carboxylate terminal groups control the properties of the monolayer. In relation to this, it is important to realize that the alkyl chains of mercaptoacids similar to the one studied here simulate the properties of the ionic barrier of the lipidic double layer of biological membranes and contribute to establishing the orientation of proteins with enzymatic activity. Therefore, monolayers of chemiadsorbed mercaptoacids may be of relevance in the preparation of biocompatible surfaces.

**EXPERIMENTAL**

Colloidal silver solutions were prepared in deionized and triply distilled water according to the method described by Creighton et al. One volume of 10−3M AgNO3 is added to three volumes of 2 × 10−3M NaBH4, previously cooled to a temperature of between 0 and 5°C, dropwise and with strong agitation. This is a transparent, yellow solution, with a maximum in its absorption spectrum at 390 nm. The adsorbate is then added to the colloid as an aqueous solution to obtain the desired concentration (10−3M) and it is observed that little variations of the concentration of adsorbate do not produce significant changes in the relative intensities of SERS bands. Raman spectra were recorded with a Jobin-Yvon U-1000 double monochromator spectrometer fitted with a cooled Hamamatsu R943–02 photomultiplier, using the 514.5-nm exciting line from a Spectra Physics gas laser. A constant slit width was used that allowed a spectral resolution of 4 cm−1; the laser power reaching the sample was always 60 mW.

**RESULTS AND DISCUSSION**

The majority chemical species present in the aqueous solutions of the here-studied mercaptoacid are, in order of increasing basicity, as follows:

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\begin{align*}
\text{HS—CH₂—COOH} & \quad \text{(I)} \\
\text{HS—CH₂—COO⁻} & \quad \text{(II)} \\
\text{―S—CH₂—COO⁻} & \quad \text{(III)}
\end{align*}
\]

Moreover, the species ―S—CH₂—COOH (IV) may exist adsorbed on the metal surface if the interaction S—Ag is stronger than the O—Ag one. The pKₐ₁ of MAA, is 3.68 and the pKₐ₂ is unknown, but Raman spectra show that the concentration of the respective species (II) is still significant at pH 11. Figure 1 shows the Raman spectra of pure MAA (a) and aqueous 1M solutions of MAA at pH 5 (b) and pH 14 (c), respectively. At pH 5 the majority species is (II) while at pH 14 it is (III) in turn. The SERS spectra of MAA have been recorded under different conditions of acidity. It is to be stressed that two different types of SERS spectra arise. Figure 1 shows also significant records obtained from 10−3M solutions at pH 5 (d) and pH 11 (e).

Table I shows the empirical assignments of the Raman spectra of pure MAA and its solutions on the basis of previous studies on related compounds such as acetic acid and sodium acetate, chloracetic acid, and alkanethiols as well as on the SERS results themselves. The assignments have been proposed taking into account the frequency shifts originated by the dissociation and the adsorption of the SH and COOH groups, but without paying attention to the possible existence of rotational isomers due to internal rotation around the S—C bond (Figure 1, inset). These kind of isomers cannot be differentiated, given that the internal rotation around C—S bonds in alkanethiols and cysteine is not sufficiently hindered at room temperature.

The band observed at 420 cm−1 in the Raman spectrum of pure MAA appears at 440 cm−1 in the spectrum of aqueous solution at pH 5 and does not shift noticeably if pH increases. It can be satisfactorily correlated with that recorded in the Raman spectra of acetic and chloracetic acids at 448 and 432 cm−1, respectively, and with that recorded in turn in the spectra of their salts at 474 and 436 cm−1, respectively, assigned to δ(COO)/μ(OCCO). The strong band recorded at 584 cm−1 in the Raman spectrum of pure MAA is observed at 598 cm−1 in the spectrum of its solutions at pH > 4. It is related to those recorded at 602 and 626 cm−1 in the spectra of acetic acid and sodium acetate, respectively, and assigned to γ(CCO) and ω(OCCO), respectively. δ(OCCO) vibrations are recorded at 678 and 708 cm−1 in MAA and its ions, respectively, which means that the dissociation of the carboxylic groups gives rise to a frequency shift amounting to Δ = 30 cm−1. In the case of chloracetic acid and its anion they are recorded at 680 and 704 cm−1, respectively (Δ = 24 cm−1).
The assignment of the vibrations $\delta$(SH), $\nu$(CS), and $\rho$(CH$_2$) is not easy because they must appear in a narrow range of frequencies. Given that the strongest band in all the SERS of alkanethiols is assigned to $\nu$(CS), it allows us to assign this mode to the bands observed at 762 and 768 cm$^{-1}$ in the records obtained at pH 5 and 11, respectively. It is in turn recorded at 788 cm$^{-1}$ in the Raman spectra of the pure acid. Moreover, the observed red-shifts in SERS, $\Delta$=26–20 cm$^{-1}$, agree satisfactorily with that observed in 1-propanethiol and 1-butanethiol, depending on whether the G or T conformer is concerned ($\Delta$=31–39 and 23–30 cm$^{-1}$), respectively.6–9 T and G conformers in these molecules are related to the internal rotation around the C(S)C(alkyl) bond, which is absent in MAA. A shoulder is recorded at 740 cm$^{-1}$ in the Raman spectrum of the pure acid and its solutions up to pH 11, and then it disappears at pH 14, and the same behavior is shown by the band recorded at 772 cm$^{-1}$. One could be assigned to $\delta$(SH), probably the latter one given that this mode is observed at 791 cm$^{-1}$ in the G conformer of 1-propanethiol and at 811 cm$^{-1}$ in its T conformer.6 Finally, the strong band observed even under drastic basic conditions at ca. 820 cm$^{-1}$ should be assigned to $\rho$(CH$_2$) by exclusion.

A strong band is observed at 910 cm$^{-1}$ in the Raman spectrum of pure MAA, which appears in turn at 943 cm$^{-1}$ ($\Delta$=33 cm$^{-1}$) in the spectrum of the aqueous solution at pH 14. It has been assigned to $\nu$(CC) given that this particular mode appears in the spectrum of acetic acid and its basic solution at 895 and 930 cm$^{-1}$, respectively ($\Delta$=35 cm$^{-1}$),17,18 while in chloracetic acid and its salt it is recorded at 911 and 931 cm$^{-1}$, respectively ($\Delta$=20 cm$^{-1}$).19

The weak bands observed at 1162 and 1247 cm$^{-1}$ in the spectrum of the pure acid and at 1138 and 1223 cm$^{-1}$ in the spectrum of its solution at pH 14 have been assigned to tw(CH$_2$) and $\omega$(CH$_2$), respectively.21 The broad bands at 1296 and 1400 cm$^{-1}$ in the spectrum of pure liquid have been assigned to $\nu$(CO) and $\delta$(OH), respectively, but these modes should be

FIGURE 1 : Raman spectra of (a) pure MAA, (b) 1 M solution at pH 5, (c) 1 M solution at pH 14. SERS spectra of (d) 10$^{-3}$M solution of MAA at pH 5, (e) 10$^{-3}$M solution of MAA at pH 11. (Inset) Rotamers of MAA around the C—S bond.
strongly coupled. At pH 5, the former band disappears and that at 1400 cm\(^{-1}\) is replaced by another strong one at 1396 cm\(^{-1}\), which should be assigned to \(\nu(\text{OCO})\). Vibration \(\delta(\text{CH}_2)\) is observed always as a shoulder at some 1440 cm\(^{-1}\) and \(\gamma(\text{CAO})\) is seen at 1688 cm\(^{-1}\) in the spectrum of pure MAA.

In the high-frequencies region one can assign mode \(\nu(\text{SH})\) to its characteristic wavenumber, with 2577 cm\(^{-1}\) being the strongest band in the spectrum of pure MAA, but its intensity decreases as pH increases. However, it is still present at pH 11. Finally, the C—H stretching modes \(\nu_1(\text{CH}_2)\) and \(\nu_{as}(\text{CH}_2)\) can be assigned to the strong band at 2937 cm\(^{-1}\) and its shoulder at 2965 cm\(^{-1}\), respectively, both frequencies being unaffected by the pH.

Concerning \(\nu(\text{SH})\), none of the recorded SERS spectra shows any band which can be assigned to it, which allows us to conclude that group —SH is completely dissociated. Moreover, the strong SERS intensities of \(\nu(\text{CS})\) as well as its shift toward lower frequencies with respect to the Raman spectrum of the pure liquid (\(\Delta=20–26\) cm\(^{-1}\)) show that a strong chemical interaction exists between the sulfur atom and the metal surface. The weak and broad band recorded at 1684 cm\(^{-1}\) in the SERS spectrum at pH 5 (Figure 1d) should be assigned to \(\nu(\text{C}==\text{O})\), while the weak band at 906 cm\(^{-1}\) corresponds with that at 910 cm\(^{-1}\) (\(\nu(\text{CC})\)) in the spectrum of pure MAA, which supports the presence of the carboxylic group. On the other hand, the SERS bands at 428, 570, 662, and 1247 cm\(^{-1}\) are satisfactorily correlated with Raman bands of the pure acid but are not present in the spectra of the ionic species (II) and (III). Under these acidity conditions, MAA is adsorbed on the silver surface through the previously deprotonated sulfur atom by formation of a S—Ag bond, while the carboxylic group remains unperturbed. Therefore the ion (IV) is the chemical species bonded to the metal and the adsorption apparently diminishes the strength of the acid group in MAA. The weak SERS intensities of vibration \(\nu(\text{CC})\) at 906 cm\(^{-1}\) suggests that the C—O bond is oriented parallel to the metal surface.\(^{22}\)

The SERS spectrum recorded at pH 11 (Figure 1e) shows some significant differences with respect to that recorded at pH 5: mode \(\nu(\text{C}==\text{O})\) is not observed, and the set of bands at 442, 580, 702, 940, and 1215 cm\(^{-1}\) correlates with Raman bands recorded at very close frequencies at pH 14, which correspond to the dianion (III). That set of bands could also be correlated with the spectrum of species (II), but this possibility is discarded provided that mode \(\nu(\text{SH})\) is not observed. On the other hand, the band assigned to \(\nu_2(\text{OCO})\) is neither enhanced nor shifted toward low frequencies, which points out that MAA continues to interact with the metal only through the sulfur atom, irrespective of the carboxylic group being as carboxy-
ylate at that pH. It is to be noticed that the behavior of acetic acid and MAA in silver sols is quite different: the former undergoes chemical transformations which originate an anomalous SERS spectrum already studied in detail by us,\textsuperscript{23} but MAA is always adsorbed as one of its ionic forms without any evidence of decomposition or chemical reaction.

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