SERS as a probe for adsorbate orientation on silver nanoclusters

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Surface-enhanced Raman scattering (SERS) spectroscopy has been used to characterize multilayers of three isomeric aromatic compounds adsorbed on silver nanoclusters. The three structural isomers, all of which adsorb in the carboxylate form onto the silver nanoclusters, bind in two different geometries to the silver surface. Different molecular configurations correlate to differences in bonding strength of these molecules to the silver surface, which can be probed by SERS. For ortho-hydroxybenzoic acid (salicylic acid), we observed red shifts of major SERS peaks in comparison to the normal Raman vibrations of nonadsorbed crystalline material. For this molecule the steric hindrance between the adjacent carboxylate and hydroxyl groups causes the carboxylate group to rotate from the common flat geometry of benzene substituents on surfaces and bond directly through one of the oxygen atoms to the surface. In this case, strong coordinative bonding between the carboxylate group and the metal surface causes the red shifts in the SERS peaks. For para-, and meta-hydroxybenzoic acid, the steric hindrance is less likely since the two functional groups are not at adjacent positions, and therefore these molecules adsorb on the silver surface in a totally flat geometry. For these molecules, in contrast to the ortho isomer, the CO2 interacts with the surface through an extended π bond, and these molecules are physically adsorbed in the common flat position. Therefore, for the meta and para substituents, we do not observe significant red shifts in the SERS spectrum. Copyright © 2009 John Wiley & Sons, Ltd.

Introduction

Surface-enhanced Raman scattering (SERS), which was discovered in 1970,[1,2] enables detection of even weak Raman vibrations due to the SERS enhancement. This enhancement, as many experiments show,[3,4] occurs as a result of the presence of a metal surface and contains two components: electromagnetic[5,6] and chemical.[7–9] Since the discovery of SERS, a vast literature concerning this effect has been published using different metal (gold, silver and copper[10–14]) substrates and ways to create SERS enhancements including aggregated metal colloids,[13,15] metal island films,[16] electrochemically roughened electrodes, and metal colloidal monolayers.[13,14]

One of the most important applications of SERS has been in the spectroscopy of organic self-assembled monolayers (SAMS), which have drawn much attention since they may provide a useful method of tailoring physiochemical properties of surfaces to various technical applications in biosensing, nanopatterning, and fabrication of molecular electronic devices.[17,18] In particular, aromatic carboxylates such as mercaptobenzoic acid (MBA) have proved to be useful for detection of different explosives.[19–21] SERS has proved to be one of the most sensitive techniques for monitoring adsorbates of short aromatic molecules on metal substrates and phenyl-containing peptides at the submonolayer coverage limit.[5,6,22–27] An exciting recent development is the ability to get single-molecule detection or Raman enhancements of up to 1015 by creating metal nanostructures or "hot spots".[28,29]

In order to analyze the shifts in the SERS spectrum, one must consider the two modes of enhancement responsible for SERS. The electromagnetic (EM) component, which is the major SERS enhancement factor, occurs as a result of the excitation of surface plasmons in a metal nanocluster, whereas the chemical component occurs because of molecular interactions between the metal surface and the adsorbate. This chemical component causes weaker SERS enhancement and may further lead to wavenumber shifts of some of the molecular Raman vibrations.

In order to analyze the influence of chemical enhancement on the SERS spectra, one needs to consider two different possible interactions between the adsorbate and the metal surface. Physical adsorption, which is the result of relatively weak interactions between the solid surface and the adsorbate with an enthalpy of adsorption higher than −25 kJ/mol, and chemical adsorption, where the adsorbed molecules are strongly bound to the surface with an enthalpy of adsorption lower than −40 kJ/mol.[30,31] In the process of chemisorption, the adsorbed molecule changes its chemical structure and symmetry because of bond formation with the surface. This mechanism usually introduces wavenumber shifts[32] between vibrations of adsorbed molecules in comparison to the normal Raman spectrum of these molecules as shown, for instance, for C60 adsorbed on noble metals,[33] and for thiophenol adsorbed on gold colloids.[34] Generally, on a silver surface chemisorption can take place through the formation of

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[28,29]
a bond between the Ag surface and an adsorbed molecule, e.g. Ag–N, Ag–O, Ag–S, or Ag–X (X = halogen) bond.[35–37]

In this paper we show that wavenumber shifts in the SERS spectrum can be correlated to specific molecular bonding geometries. The relationship between molecular configuration and the specific binding mechanisms inferred from the wavenumber shifts enables us to identify surface geometries of three different aromatic molecules adsorbed on metallic surfaces, and may be implemented to several other adsorbed molecules.

SERS has been used previously for determining the orientation of molecules adsorbed on certain surfaces.[38–41] The SERS spectra of many aromatic carboxylic acids have shown that the acid is adsorbed on the surface as a carboxylate ion.[39,40,42–44] This carboxylate species binds to the metal surface via either the oxygen lone pair electrons or the carboxylate π system.[45] The geometry of the carboxylates on the surface, which is dictated by steric hindrance between the carboxylates and other adjacent substituents, determines the nature of binding of these molecules on the surface.

Suh and Kim[42] identified three different binding geometries for aromatic carboxylates adsorbed on surfaces, depending on the relative position between the carboxylate and other substituents on the aromatic ring. The flat geometry, where the ring as well as the carboxylate and the other substituent lie entirely flat on the surface and the carboxylate binds to the surface through its π-electrons, is usually observed in para substituted molecules or in meta substituents. In the one-legged geometry, the carboxylate rotates from the plane of the ring as a result of steric hindrance between adjacent substituents, and only one oxygen of the COO− group binds strongly through its oxygen lone pair electrons to the surface. This geometry is observed with mostortho substituents. The third geometry, which is not observed with the molecules in this study, is the two-legged geometry in which the COO− is adsorbed to the metal surface through both of its oxygen atoms and the ring is tilted with respect to the surface. In an earlier paper it was shown[46] that the different geometries can be detected by the relative intensities of the carboxylate bending/stretching vibrations.

In this paper we show that the nature of the adsorbate–surface bonding can also be detected by the wavenumber shifts in the SERS spectrum[46] in comparison to the bulk crystalline Raman spectrum of the same molecule. Therefore, we compare the SERS and Raman spectrum of three isomers: para, meta, and ortho-hydroxybenzoic acid, with the carboxylate and hydroxyl groups at different relative positions (Fig. 1).

For the ortho isomer, we observed wavenumber shifts between the Raman and SERS spectrum points to chemical adsorption and therefore a one legged geometry, in which the oxygen binds strongly to the silver nanocluster, while for the meta and para isomers no wavenumber shifts are observed because of weaker physical adsorption (π bonding) typical of the flat geometry.

![Molecular structures of para-hydroxybenzoic acid, meta-hydroxybenzoic acid, and ortho-hydroxybenzoic acid.](image_url)

**Figure 1.** Molecular structures of para-hydroxybenzoic acid, meta-hydroxybenzoic acid, and ortho-hydroxybenzoic acid.

**Experimental**

In the SERS experiments we used silver island films of 10–15 nm thickness, which were vacuum deposited onto a glass surface. The glass microscope slides were cleaned mechanically with soap and water, rinsed with ethanol, and dried in an air stream. The silver deposition was carried out in a vacuum bell jar maintained at ∼10−6 torr via resistive heating evaporation from an alumina-coated molybdenum boat containing silver wire of 99.99% purity. The clean glass samples were generally 10 cm above the evaporation boat. After deposition of the silver, the samples were annealed in a hydrogen atmosphere at 200 °C for about 45 min. The annealing process causes the silver particles to aggregate into a film composed of isolated nanoclusters, which is crucial for the SERS measurements. The silver cluster morphology was examined using a Nanoscope III (Digital Instruments) atomic force microscope (AFM), and the optical absorptions spectra of the film were measured by a Cary 500 scan UV–vis–NIR spectrophotometer. The crystallinity of the silver clusters was examined with a Bruker AXS D8 Advance Diffractometer (using Cu Kα, λ = 1.5418 Å radiation) operating at 40 kV/40 mA and equipped with a graphite-reflected beam monochromator and variable divergence slits for powder X-ray diffraction analysis.

After examining the morphology and optical absorption spectra of the films, we covered the films with multilayers of the aromatic molecules by spin coating (10 μl of diluted solution (10–100 mM) of each molecule in ethanol, starting with 5 s at 500 rpm and followed by 50 s at 5000 rpm). Therefore, we can estimate that roughly 1 × 1010 molecules/cm2 (100 molecules/μm2) are adsorbed on the silver films. For the bulk Raman measurements we used powder crystalline samples (as purchased) of the aromatic compounds. In all cases analytical grade reagents (>99.9%) (Aldrich – Sigma) were used. Raman and SERS measurements were made on a customized Raman microscope that includes a modified Leica DMLM microscope with a DFC 280 camera, an IHR320 imaging spectrometer with a cooled 1024 × 256 pixel CCD (Symphony). Raman and SERS excitation was with a 532-nm diode-pumped solid state laser (1.2 mW, 4 μm spot size, 100× objective, 20 s single spectral scan). In order to confirm the results, Raman and SERS measurements were repeated several times for each sample and on a number of substrates.

**Results and Discussion**

The SERS substrates were first examined by AFM (Fig. 2), optical absorption spectra, and X-Ray diffraction in order to determine the quality, crystallinity, size, and absorption of the annealed silver nanoclusters. From the AFM scans we were able to determine that the average particle size was ~60 nm; the optical absorption spectral measurements clearly showed the silver plasmon resonance at ~410 nm wavelength; and the XRD pattern revealed polycrystalline silver clusters oriented in the (110) axis on the glass substrate.

In order to examine the nature of binding of the different aromatic molecules (ortho-, meta-, and para-hydroxybenzoic acid) (Fig. 1) on the silver nanoclusters, we compared their bulk Raman and SERS spectrum. The bulk Raman and SERS spectra are presented in the ~600–1800 cm−1 region, which contains the main Raman peaks of these molecules. In general, broadening is not an SERS phenomenon; nevertheless, in SERS the molecule may change its identity upon adsorption and become a surface...
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Figure 2. AFM scan of the SERS substrate showing the silver nanoclusters.

Figure 3. Bulk Raman (black) and SERS (gray) spectra for ortho-hydroxybenzoic acid with 532 nm excitation wavelength.

complex. This may result in small shift and/or broadening of the Raman peaks.[47]

SERS and Raman measurements for ortho-hydroxybenzoic acid are shown in Fig. 3. The three peaks at 1630, 1580, and 1025 cm\(^{-1}\) are assigned to the \(\nu_8b\), \(\nu_8a\), and \(\delta_{18b}\) aromatic ring vibrations, respectively (Table 1), referring to the works of Varsanyi.[48] As seen from Fig. 3, these three vibrations have a red shift in the peak position of \(\sim20–35\) cm\(^{-1}\) between the bulk Raman and SERS spectrum. To further explore the origin of this shift, we examined the bulk Raman and SERS spectra of the other two isomers. Figures 4 and 5 show the comparative bulk Raman and SERS spectra of para- and meta-hydroxybenzoic acid, respectively. Unlike the red-shifted aromatic ring vibrations of ortho-hydroxybenzoic acid, in para- and meta-hydroxybenzoic acid spectra the aromatic ring vibrations are nearly unshifted (Table 1).

At the molecular concentrations used in the SERS experiments, the ordinary Raman spectrum of all three molecules is completely

Table 1. Peak wavenumbers (in cm\(^{-1}\)) and their assignments for the observed Raman and SERS spectra of ortho-, para-, and meta-hydroxybenzoic acid.[48]

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unobservable and it is only the enhancement by the silver nanoclusters that allows the observation of the SERS spectrum, thus implying that all three molecules lie on the surface in close proximity to the silver clusters. Therefore the differences observed between the SERS and Raman spectra for the three molecules can only be due to the bonding strength and bonding nature between the silver cluster and the various aromatic molecules.

From the Raman and SERS measurements we can identify the following: First, in all three molecules we can identify that the carboxylate species is adsorbed on the surface, and not the carboxyl. For adsorbed ortho-hydroxybenzoic acid we observe the CO$_2^-$ bands at approximately 1385 and 850 cm$^{-1}$.[42] In the bulk Raman spectrum of ortho-hydroxybenzoic acid we also observe a weak CO$_2^-$ band at 1382 cm$^{-1}$, which is unexpected since the crystals of all three isomers are in the acid form.[49–51] Nonetheless, this is probably due to a small amount of deprotonation that occurs at the bulk surface when the crystal is exposed to moistened air. In the para-hydroxybenzoic acid SERS spectrum, the CO$_2^-$ bands are at 1360 and 850 cm$^{-1}$. For meta-hydroxybenzoic acid, we observe the CO$_2^-$ bands at 1360 and 860 cm$^{-1}$. Additionally, the ortho-hydroxybenzoic acid $\nu_3$ band at 768 cm$^{-1}$ in the Raman spectrum is shifted to 670 cm$^{-1}$ in the SERS spectrum, which is also indicative of carboxylate formation, as reported by Varsanyi.[48]

Second, all three molecules bind with the benzene ring adsorbed flat on the silver surface, which can be deduced from the absence of the C–H aromatic stretch in the SERS spectrum at $\sim$3000 cm$^{-1}$ (not shown in the graphs) due to SERS selection rules.[42]

$\alpha$-Hydroxybenzoic acid is similar to thiosaliclycic acid[42] and therefore expected to bind in a one-legged geometry because of steric hindrance between the CO$_2^-$ and OH bulky groups (Fig. 6). In the SERS spectrum of ortho-hydroxybenzoic acid (Fig. 3) the $\rho_3$ CO$_2$ band at 850 cm$^{-1}$ is sharp and stronger than the $\nu_5$ (COO$^-$) band at 1385 cm$^{-1}$, which confirms the adsorption of only one oxygen of the CO$_2^-$ group in the one-legged geometry by the method of Suh and Kim.[42] The vibration at 1025 cm$^{-1}$ in the bulk Raman spectrum, which is shifted to 990 cm$^{-1}$ in the SERS spectrum, is assigned to the $\delta$(CCC) + $\rho_3$ CO$_2$ $\nu_1ab$ in-plane bending vibration, and is most shifted as a result of the strong coordinative binding between one of the CO$_2^-$ oxygen lone pairs to the silver surface when the carboxylate is rotated from the molecular plane. This binding between the metal and ligand involves charge transfer,[52,53] which is part of the chemical enhancement mechanism and is responsible for the red shift in the SERS spectrum. Two other peaks at 1630 and 1580 cm$^{-1}$ in the bulk-Raman spectrum are shifted to 1600 and 1565 cm$^{-1}$, respectively, in the SERS spectrum. These two peaks are assigned to the $\nu_{8b}$ and $\nu_{8a}$ vibrations, respectively,[48] and are the aromatic ring vibrations that are most affected by the chemical adsorption of the carboxylate group and are therefore red-shifted.

Conversely, $\alpha$-hydroxybenzoic acid binds in a totally flat geometry, similar to $\alpha$-aminobenzoic acid[42] (Fig. 6). For the $\delta_{8a}$ in-plane bending vibration and the $\nu_{8a}$ aromatic ring vibrations at 1160 and 1600 cm$^{-1}$, respectively (as shown in Fig. 4), no significant shifts are observed between the bulk Raman and SERS spectrum. These unshifted peaks indicate a weaker intermolecular $\pi$ bonding that does not involve substantial charge transfer, as with ortho-hydroxybenzoic acid, and therefore no substantial shifts are observed in the SERS spectrum. The typical $\nu_5$ (COO$^-$) expected at $\sim$1380 cm$^{-1}$[42,48] is, however, red-shifted to 1360 cm$^{-1}$ (Table 1) in the respective SERS spectrum, because of the physical $\pi$ bonding of the COO$^-$ on the surface, as has already been noted for other aromatic molecules that are also physically adsorbed on metallic surfaces.[46] Moreover, in the SERS spectrum the $\rho_3$ CO$_2$ band at 850 cm$^{-1}$ and the $\nu_5$ (COO$^-$) band at 1360 cm$^{-1}$ are both strong, which makes it difficult to determine the surface geometry by Suh’s convention.[42] Usually we would expect strong $\nu_5$ (COO$^-$) and weak $\rho_3$ CO$_2$ bands in a flat geometry.[42] In our case, the strong $\delta$ (COO$^-$) is observed probably as a result of the overlap between the $\delta$ (COO$^-$) and the $\rho_1$ CH vibrations (Table 2), which results in a strong broad band at 850 cm$^{-1}$, and therefore makes it difficult to use the SERS signal intensity for determining surface geometry as was done by Suh and Kim.[42] Here, the absence of large red shifts in the ring vibrations is good evidence for physical adsorption and a flat geometry.

$m$-Hydroxybenzoic acid also binds in a totally flat geometry (Fig. 6) and does not coordinate with the carboxylate oxygens, as can be seen with the $\nu_{8b}$ and $\nu_{12}$ SERS strong bands at 1603 and 997 cm$^{-1}$, respectively, which remain nearly identical as in the bulk Raman spectrum (Fig. 5). This is again supported by the work of Suh and Kim,[42] where in the SERS spectrum of $m$-
hydroxybenzoic acid (Fig. 3) the δ (COO\(^-\)) band at 860 cm\(^{-1}\) is weak compared to the strong vs (COO\(^-\)) band at 1360 cm\(^{-1}\), which confirms the adsorption in a flat geometry. Again, the typical \(v_\text{r}(\text{COO}^-)\) expected at \(\sim 1380 \text{ cm}^{-1}\)\(^{42,48}\) is red-shifted to 1360 cm\(^{-1}\) (Table 1) in the respective SERS spectrum because of the physical π bonding of the COO\(^-\) on the surface, as with the para isomer. Moreover, small shifts (5 cm\(^{-1}\)) are observed between the bulk Raman and SERS spectra, which are also characteristic of physical π bonding\(^{46}\) and not chemical adsorption. In contrast to the ortho isomer, meta-hydroxybenzoic acid lacks steric hindrance and is similar to the para isomer, and therefore binds in the totally flat geometry.

**Conclusion**

In summary, the chemical enhancement component of the overall SERS enhancement is associated with chemical interactions between the metal and the adsorbate, which can also affect some of the vibrational wavenumbers of the adsorbed molecules. Chemical adsorption accompanied by charge transfer between the metal and the ligand as for para-hydroxybenzoic acid causes substantial red shifts of some of the Raman bands. When the adsorption is through a weaker intermolecular π bonding, as for meta- and para-hydroxybenzoic acid, the SERS spectrum remains nearly identical to the bulk Raman spectrum. By comparing with the recent work on the geometries of surface-adsorbed carbonyl groups, which has correlated between molecular configuration and surface binding, we have been able to correlate between molecular configuration and red shifts in the SERS spectrum. The determination of the molecular orientation on the surface is based on the differences in the type of binding of the molecules to the silver clusters, which affects the position of some vibrational peaks in the molecular SERS spectrum. Peaks that are red-shifted when strong chemical interaction occurs, as with ortho-hydroxybenzoic acid, are usually associated with vibrations that are closely coupled to the coordinative bond of the molecule, as with the δCCC + ρCCO\(^-\), which is in close proximity to the carboxylate metal bond. Other vibrations, such as the \(v_{\text{BB}}\) ring vibration, are often affected by chemical adsorption of the molecule and are frequently red-shifted when chemical interactions occur.

**References**