Use of Self-Assembled Monolayers of Alkyl Mercaptans To Investigate the Chemisorption and Photochemistry of *p*-Nitrobenzoic Acid on Silver Islands

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Surface-enhanced Raman spectra were obtained from *p*-nitrobenzoic acid (PNBA) adsorbed onto silver island films that had previously been coated with self-assembled monolayers of alkyl mercaptans. PNBA adsorbed onto silver as a *p*-nitrobenzoate ion, penetrating through the hydrocarbon layer. However, the alkyl coating hindered the chemisorption and revealed the existence and location of two types of adsorption sites. The photo-induced reduction of PNBA[1,2] was not observable when the molecule was adsorbed on silver previously coated with hexadecyl mercaptan. In general, the reaction was much slower when silver was coated with hydrophobic layers than when it was bare or coated with hydrophilic layers. These results are discussed and interpreted in favor of a polymolecular mechanism for the photoinduced reaction.

Introduction

Here, we expose the combined use of a recently developed technique, surface-enhanced Raman scattering, and of self-assembled monolayers to get information on the chemisorption and chemical reaction of a molecule on silver. Surface-enhanced Raman scattering (SERS)[3–5] is a phenomenon occurring at a rough surface of a good metallic conductor. Raman signal from molecules at the surface is 10^3 to 10^6 times more intense than that from molecules in a bulk sample. Thus, the SERS phenomenon has been developed[5] as a nondestructive technique able to give directly and selectively interfacial chemical information. When a thick (up to 1 μm) layer of organic material was deposited on a rough silver surface, a Raman signal collected from this sample was dominated by the scattering of molecules adsorbed directly onto silver.[5]

Among the applications of this developing technique, promising work has been done in the area of surface chemistry and catalysis. However, SERS is known to induce some artifacts. Among them, the most prominent is enhanced photochemistry at the metal–organic interface. This was treated theoretically by Nitzan and co-workers[6] within the frame of a purely electromagnetic theory for SERS. Enhanced reactions can also be explained with the so-called "chemical" charge-transfer mechanism.[2] An example of chemical reaction occurring during the collection of SERS data is the photofragmentation and graphitization of hydrocarbon molecules.[7]

p-Nitrobenzoic acid (hereafter named PNBA) was used as a scatterer in many SERS experiments[8] before it was recognized that the molecule underwent a chemical reaction due to the laser illumination.[1,2] At a low laser power, the SERS spectrum of PNBA (Figure 1b) was very similar to the normal Raman spectrum of *p*-nitrobenzoate ions in solution (Figure 1c). When the sample was illuminated with a higher power, the spectrum changed. The new spectrum revealed the appearance of a new molecule. Roth et al. showed that this product was probably azodibenzoate.[1] Sun et al.[2] showed that the maximum rate of reaction was obtained at the same wavelength, about 500 nm,

as the maximum SERS intensity. They also observed that the reaction had an electrochemical behavior. Sun and co-workers stated that the new molecule was either *p*-aminobenzoate or azodibenzoate or both, relying on the similarity of the spectra of the nitro and amino compounds. However, Venkatachalam et al. showed that *p*-aminobenzoic acid, when chemisorbed on rough silver, also underwent a reaction.[9] The initial spectrum was similar to that of *p*-aminobenzoate, but exposure to air and water vapor induced a reaction with the same final product as what was found in the case of PNBA. It is noteworthy that the normal Raman and SERS spectra of azodibenzoate resembled one another and were both very similar to the SERS spectrum of the reaction product.[2,9] It seems thus very likely that the product of the photoinduced reduction of PNBA was azodibenzoate, which in turn seemed to be stable during SERS experiments. It was also noticed that photoinduced reduction of two nitro groups into an azo bond was quicker under nitrogen than in ambient air.[10] Thus it seems that oxygen hindered the reaction of nitro compounds and that atmospheric moisture was not involved in the reaction process, contrary to what is seen for amino compounds. However, the exact reaction process is not known and deserves some more investigation. Finally, we have to stress that this photoinduced reaction is not restricted to rough silver surfaces.[11] We observed the same reaction when PNBA was deposited on a smooth silver surface.

Here, we present further information about the PNBA/silver system, obtained by chemically modifying the surface of silver. Self-assembled monolayers of alkyl mercaptans can be deposited on silver and gold.[12] A sulfur–metal bond is formed. Adsorption and catalysis at the metallic surface are totally transformed. On smooth and flat substrates, alkyl mercaptans can provide a very uniform coating, especially when the alkyl chain has 12 carbon atoms or more. On rough silver, we first used them as spacer layers in order to investigate the dependence of the SERS effect on the distance from silver.[13] We found that PNBA penetrated inside the alkyl chains and could chemisorb on silver. Here, we show how these layers modified the environment of the adsorbate and the surface chemistry. Deductions about the chemisorption and reduction reaction can be made from these observations. It is probable that the monolayer of alkyl

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mercaptans only left uncovered convex surface sites, i.e., kinks between flatter areas of the surface. We interpret our data with this main idea and present some evidence for it. Another possible explanation of PNBA adsorption results is that the sites not covered by mercaptans have a weak reactivity with respect to mercaptans. However, the results obtained for the reduction reaction are in favor of the geometrical interpretation with convex sites. Due to the inertness of alkyl chains and to the good coverage of silver by alkyl mercaptans, we think that this method could be applied to a number of other systems in surface chemistry on rough surfaces. About 20 years ago, Hertl and Hair[14] exploited a similar idea. They used monochlorotrimethylsilane to study and modify the adsorption sites of water on colloidal silica. They interpreted their results with a discussion of surface functional groups only. Due to the nature of the organic tail of the silane (three methyl groups), their coating was probably not sensitive to surface roughness.

Materials and Methods

Methods for Raman spectroscopy and preparation of silver island films were fully described elsewhere.[13] The poor adhesion of silver on the substrate is the main physical reason for the formation of metallic aggregates during deposition. Thus, silver island films were fragile and sensitive to environmental attacks. For example, soaking in a solvent can decrease the SERS capacity of the films, probably by rinsing out some of the aggregates. Moreover, exposure to the atmosphere induced the contamination of the surface of silver; adsorption on silver was modified by the presence of the pollution layer. For these reasons, silver films were used for adsorption or Raman analysis immediately after being taken from the vacuum deposition system. A 5145 Å argon ion laser was used to obtain Raman spectra.

p-Nitrobenzoic acid (PNBA) was purchased from Eastman and was 98% pure. Absolute ethanol was obtained from Midwest Grain. The *n*-alkyl mercaptans were purchased from Aldrich; octyl mercaptan (OCM, 8 carbons) was 98% pure, dodecyl mercaptan (DDM, 12 carbons) 98% pure, and hexadecyl mercaptan (HDM, 16 carbons) 92% pure. Mercaptoundecanoic acid (MUA, 11 carbons) was synthesized from bromoundecanoic acid (Aldrich), with sodium metal and thioacetic acid (Aldrich), following a recipe available in the literature.[15] PNBA was deposited by spin-coating on bare and covered silver island films from a 0.001 M solution in ethanol. In both cases, the spinner was used at 2000 rpm during about 30 s. On higher energy surfaces (bare silver or silver covered with MUA), this concentration was enough to yield a layer several molecules in thickness, but the film was thin enough to give no measurable normal (bulk) Raman signal in the usual experimental conditions.

Self-Assembled Monolayers of Mercaptans. We used *n*-alkyl mercaptans to obtain hydrophobic coatings of low surface energy and an *ω*-terminated alkyl mercaptan, mercaptoundecanoic acid, to get a hydrophilic coating of higher surface energy. Self-assembled monolayers (SAM) of alkyl mercaptans on silver films were adsorbed from 10^{-2} M solutions of the mercaptans in absolute ethanol. Silver island films on glass were taken out of the vacuum system and immediately dipped into the solution. The adsorption lasted from a few minutes to several hours with very few changes in the spectra of the thiols alone and no change in the peaks assigned to PNBA. The quickness of the adsorption was already noticed by other authors for hydrophobic[12a,15] or hydrophilic coatings.[15] After adsorption, the samples were rinsed with ethanol and dried with an inert gas stream. The spectra were taken a few hours after the
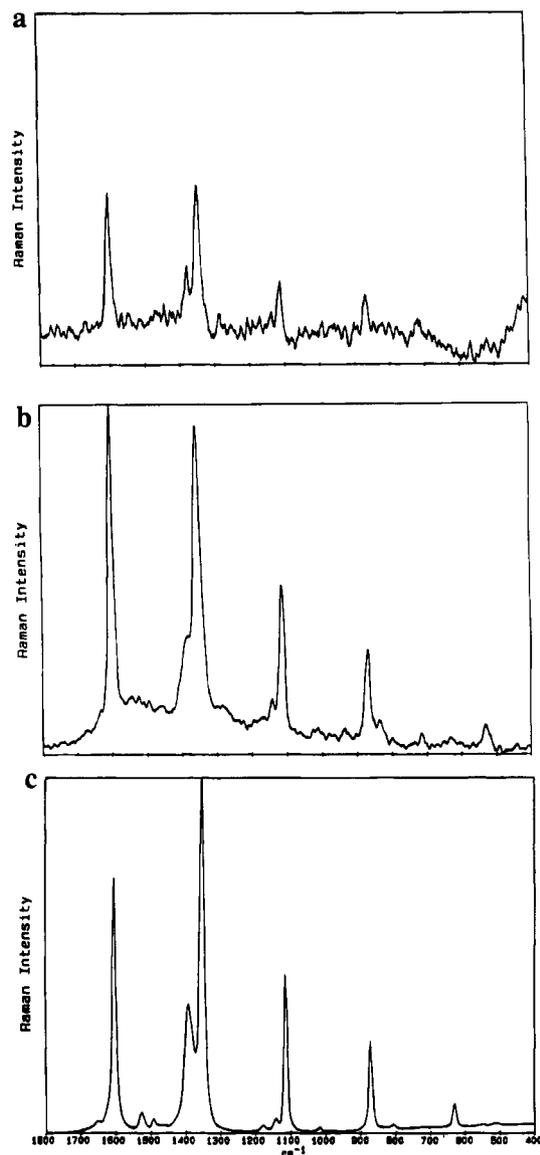

Figure 1. Raman spectra of *p*-nitrobenzoic acid (PNBA). (a) SERS of PNBA deposited on a silver island film previously coated by a SAM of *n*-hexadecyl mercaptan (HDM); the spectrum of HDM has been subtracted. The power was 20 mW at the sample. (b) SERS of PNBA on bare silver island film, at a lower power, about 0.25 mW at the sample. (c) Bulk Raman spectrum of PNBA in concentrated NaOH. The molecules are ionized in benzoate ions. The resolution is 15 cm^{-1} in a and b and 10 cm^{-1} in c.

adsorption was performed. Details about the SERS spectra of alkyl mercaptans can be found elsewhere.[13] In ref 13, we also discuss in detail the coverage of silver by the mercaptans. Coverage by carboxyl-terminated mercaptans was found to be as effective as coverage by *n*-alkyl mercaptans. SAM of mercaptans are known to provide uniform layers on noble metals. However, this now well-known result concerns SAM on smooth metallic surfaces. Thus, it does not immediately apply in our case, where the roughness of island films is likely to induce some coverage defects. In fact, our results show that some small areas of silver remained available for the chemisorption of PNBA.

Results and Discussion

SERS and normal Raman spectra of PNBA are displayed in Figure 1. The spectrum of Figure 1a is that of PNBA deposited on a rough silver film coated with a monolayer of the 16-carbon

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mercaptan (HDM). For PNBA on bare silver, Figure 1b was obtained. Both can be compared to the normal, unenhanced Raman spectrum of PNBA in an aqueous solution of sodium hydroxide (Figure 1c), which was dominated by the signal of the carboxylate ions. The 1390 cm^{-1} peak of Figure 1c is due to the carboxylate symmetric stretching vibration. Carboxylic acid groups in another configuration would yield different peak positions. Dimers in the crystal gave a Raman band around 1640 cm^{-1}, whereas nondimerized, nonionized molecules showed features around 1700 cm^{-1}; for example, a weak band at 1720 cm^{-1} was observed for PNBA in ethanol. The carboxylate peak is present on bare silver, as was found earlier,[1,2] but also on mercaptan-coated silver (see Figure 1a,b). We made sure that this carboxylate was due to chemisorption onto silver and did not involve some contaminant cations. The best test was obtained by rinsing the samples with ethanol, the reverse action of the deposition technique. Physisorbed species would be dissolved and flushed away by the pure solvent. Rinsing both types of samples did not change the spectrum neither in quality nor in intensity. Thus, PNBA chemisorbed on silver by formation of a carboxylate ion through the 16-carbon alkyl layer of HDM.

The SERS spectra of PNBA were the same on silver films covered with HDM, DDM, OCM, or MUA, showing in every case direct chemisorption onto silver. No signal was obtained from PNBA physisorbed on top of the alkyl layer. This was true even for the MUA monolayer, which had a higher surface energy and thus a physisorbed PNBA layer. This observation is discussed in ref 13 and is consistent with earlier findings.[16] The only difference between the four spectra was seen in the intensity of the SERS signal. An 8-carbon layer (OCM) reduced the signal of chemisorbed PNBA by a factor of about 10 compared to bare silver films, whereas 12- and 16-carbon layers divided the signal by 15 and 25−30, respectively. This variation was the same whether the mercaptan was purely alaphatic (DDM) or had a hydrophilic end group (MUA). The spectrum of chemisorbed PNBA gives information on the coverage of rough silver by the SAM of mercaptans.[13] There is no simple relation between the SERS intensity and the surface concentration of scatterer. The relation was shown to be highly nonlinear in many cases.[17−21] However, the relation was found to be monotonic, except in the case of resonant SERS with dye molecules.[17] Thus, a weaker signal of chemisorbed PNBA is an indication of better coverage by mercaptans.[13] The longer the alkyl chain, the weaker the signal, thus, the better the coverage. This is very well understood as being due to the stabilization of the self-assembled monolayer by interactions between hydrocarbon groups.

The positions of the band maxima of Figure 1a−c given in Table 1, together with the positions for the normal Raman spectrum of crystalline PNBA. There are only two significant shifts from bare silver to silver coated with mercaptans: the maxima of the nitro and carboxylate bands shift from 1355 and about 1390 cm^{-1} to 1347 and 1380 cm^{-1} respectively. Further details on the adsorption sites were obtained by scanning the 1300−1400 cm^{-1} region of PNBA chemisorbed among a self-assembled monolayer of OCM (eight carbon atoms). Figure 2 displays a decomposition of the peaks. This manipulation shows that, on bare silver, the nitro band is made up of two single peaks at 1347 and 1357 cm^{-1} and the carboxylate band of two peaks at 1380 and 1393 cm^{-1}. The elementary peaks at 1347 and 1357 cm^{-1} have about the same width. When PNBA chemisorbed through the alkyl layer, only the 1347 cm^{-1} nitro and 1380 cm^{-1} carboxylate peaks were visible. Similar peak shifts were observed in another SERS experiment where surface

TABLE 1: Positions of the Strongest Peaks in Raman Spectra of p-Nitrobenzoic Acid[a]

location of vibrations	SERS on coated silver (Figure 1a)	SERS on bare silver (Figure 1b)	p-nitrobenzoate in NaOH solution (Figure 1c)	crystalline PNBA
phenyl	1601 s	1601 s	1604 s	1604 m
COO⁻ sym stretch	1380 m	1390 sh	1392 m	
NO₂ sym stretch	1347 s	1355 s	1353 s	1356 s
NO₂	1111 m	1114 m	1114 m	1113 m
NO₂	868 m	869 m	872 m	867 m
phenyl			631 w	633 w

[a] Positions in cm^{-1}; s = strong intensity, m = medium, sh = shoulder. Wavelength = 5145 Å; resolution was 5 cm^{-1} for normal Raman, 10 cm^{-1} for SERS.
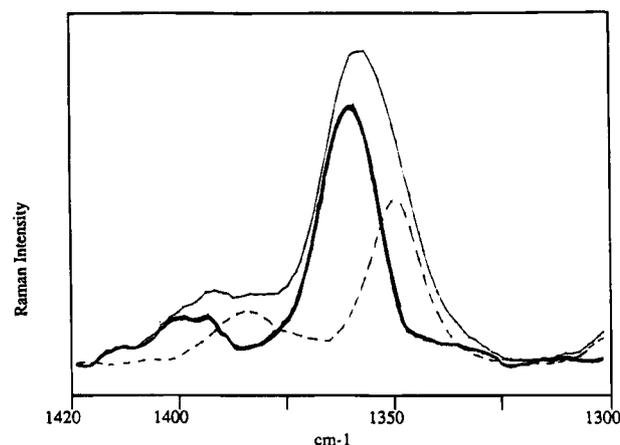

Figure 2. Carboxylate and nitro peaks of PNBA. The thin line is the spectrum on bare silver. The dashed line was taken from PNBA adsorbed on a mercaptan-coated silver film (the mercaptan is OCM). Subtraction of one from the other gives the thick line, with an ad hoc subtraction factor. This subtraction reveals the SERS spectrum on bare silver (thin line) as composed of two species, only one of them being present when PNBA adsorbs through an alkyl mercaptan layer. The 1347 and 1357 cm^{-1} peaks are assigned to the symmetric stretch of nitro, the 1380 and 1393 cm^{-1} peaks are assigned to the symmetric stretch of carboxylate groups. The resolution is 7.5 cm^{-1}.

concentration of the scatterer was varied.[18] In ref 18, the shift of the peaks was interpreted as evidence for the existence of two adsorption sites, as in our case. We already know that some of the sites that were not covered by OCM or DDM were covered by the longer chain mercaptan HDM, due to monolayer stabilization by hydrocarbon interactions. This is compatible with the geometrical argument for noncoverage (convex sites) but also with the chemical argument (weaker Ag−S bond). Before discussing the adsorption data further, we first consider the photoinduced reaction of PNBA on coated silver films.

High-power laser illumination induces a chemical change of PNBA on silver. As discussed in the introduction, the reaction product is very likely azodibenzoate. The N=N double bond would occur by combined reduction of two nitro groups. Table 2 summarizes the results of such an illumination for PNBA on coated silver surfaces, while Figure 3 presents schematic drawings of the molecular situation. Figure 4 displays a spectrum at high power of PNBA on MUA-coated silver. We could observe no reaction when PNBA was chemisorbed through a HDM layer, whatever the laser power. Table 2 shows that the reaction was slower for silver with hydrophobic coatings (OCM, DDM, or HDM) than for bare silver or silver with hydrophilic coatings (MUA). These findings reinforce the analysis that was cited in the Introduction.

TABLE 2: SERS Intensity of Chemisorbed PNBA and Rate of Reaction after Coverage of Silver by Alkyl Mercaptans

type of substrate	intensity of the 1350 cm^{-1} nitro band (normalized to the intensity on bare silver) power = 1 mW	extent of reaction after 30 min: ratio of the 1460 cm^{-1} peak to the 1350 cm^{-1} peak (normalized to bare silver) power = 20 or 50 mW^a
bare silver island film	standard: sum of both nitro peaks	standard
silver/OCM layer	$(8 \pm 2) \times 10^{-2}$	$\approx$0.2—0.4
silver/DDM layer	$(7 \pm 2) \times 10^{-2}$	$\approx$0.3
silver/HMD layer	$(3.5 \pm 0.5) \times 10^{-2}$	<0.1
silver/MUA layer	$(6 \pm 1) \times 10^{-2}$	$\approx$1

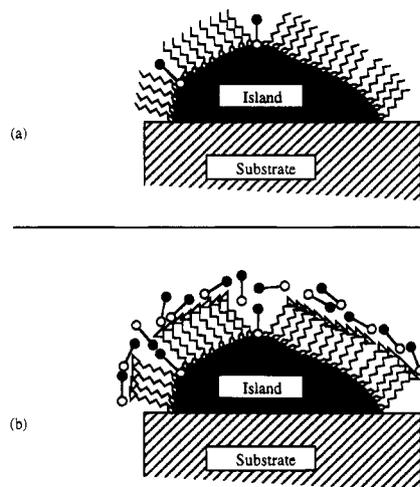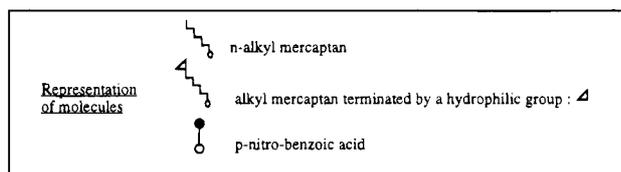^{a} 20 mW for MUA-covered silver surfaces.

Figure 3. Representations of PNBA deposited on coated silver islands. Silver island films are 45 Å in average thickness; islands are about 100 Å in height and 200 to 300 Å in lateral dimensions (ref 17). The mercaptans tend to cover better flat portions of the surface. Thus, when PNBA is later deposited, it chemisorbs on kinks. If the outer surface has a low energy, with n-alkyl mercaptan, chemisorbed PNBA molecules are rather isolated (a). The reduction reaction is hindered because it necessitates the proximity of two PNBA molecules. When the alkyl mercaptan is terminated by a hydrophilic group (MUA), PNBA physisorbs on the outer surface (b) and the reaction is much quicker.

First of all, we need to stress that the observed variation in the rate of the photoinduced reaction is not due to the difference in the adsorption sites between bare and coated silver. This is seen in the fact that MUA-coated silver has a rate much bigger than HDM-coated silver, although both display the same type of adsorbate spectrum. The reaction is possibly a complex one, and more molecules may be involved than suggested by the simplified scheme

$$\text{—NO}_2 + \text{O}_2\text{N—} \xrightarrow{\text{photons, Ag}} \text{—N=N—}$$
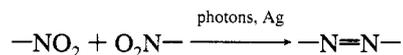
It may be that water molecules are necessary to initiate the chemical reduction. The lesser amount of available water molecules may explain the decrease in the rate of reaction when PNBA is among octyl or dodecyl chains, which are hydrophobic. This would also explain the quicker rate for PNBA in a
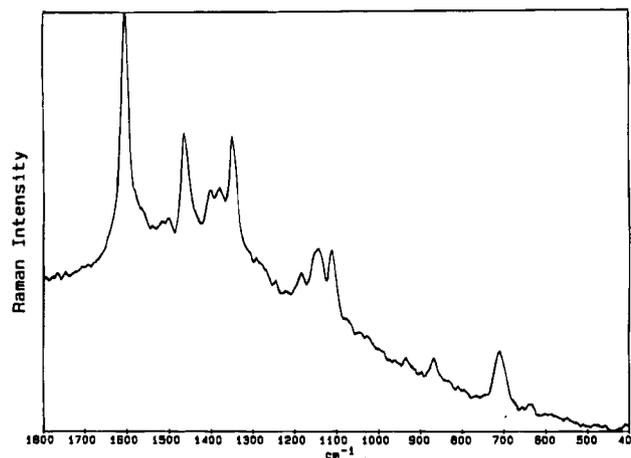

Figure 4. Spectrum of PNBA on Silver Islands with a Hydrophilic Coating. Power = 20 mW at the sample; continuous illumination during a scan at 1 cm^1/s . The spectra obtained of PNBA on bare silver are very similar. For PNBA on silver with hydrophobic coatings, the 1460 cm^{-1} peak, assigned to the azo group, is much weaker (see Table 2).

hydrophilic MUA coating than in hydrophobic coatings. But, we do not expect a radical change in the presence of water between the dodecyl and hexadecyl chains. Thus, this factor does not explain the absence of reaction for HDM coatings. Moreover, it was shown elsewhere that the absence of oxygen was more important than the presence of water for the reaction of PNBA on silver island films: quicker rates were obtained in a nitrogen environment,[10] which was drier than ambient air. In hydrophobic coatings, H$_2$O molecules were probably very scarce, but O$_2$ molecules were probably rare, too. In fact, although it is probable that a third molecule (water?) is necessary for the reaction to occur, we think that the experiments summarized in Table 2 mainly test the possibility of combination of two PNBA molecules (see Figure 3). The smaller the concentration of PNBA, the slower the reaction was. Hence, these results are compatible with the reaction product being azodibenzoate. The HDM layer, which does not prevent PNBA from chemisorbing on silver, does prevent the reduction reaction. This passivation effect is explained by the fact that two PNBA molecules cannot chemisorb one in proximity to the other. On HDM-coated rough silver, the only sites available for PNBA adsorption were isolated and able to take one molecule only (Figure 3a). For shorter-chain OCM or DDM, PNBA molecules were closer to each other than for HDM; thus the reaction was possible. Finally, for hydrophilic MUA, PNBA molecules were available in the upper physisorbed layer for a bimolecular reaction (Figure 3b).

No photoinduced reaction was detected with PNBA chemisorbed onto silver coated with HDM. This shows that the adsorption sites of PNBA were isolated. Thus the reason for the noncoverage of these sites by the self-assembled monolayer is likely to be a convex geometry. A different reactivity alone, i.e., in a flat zone, would rather induce a patch of PNBA adsorption with several molecules together, and thus, the reaction would still be present. However, a convex geometry can also be associated with a different surface chemistry. Coverage defects were likely to be found at points of the surface where the curvature radius was the smallest, possibly associated with a weak reactivity toward mercaptans. Thus, the 1347 cm^{-1} nitro and 1380 cm^{-1} carboxylate peaks were characteristic of PNBA chemisorbed on areas of small curvature radius, as depicted in Figure 3a. The peak positions on OCM-coated silver were the same as those on DDM- or HDM-coated silver. But, the signal was much lower after HDM coating (Table 2). We may think

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that the sites yielding the signal on HDM-coated silver were even rougher than those involved in the signal from OCM-coated silver. However, mercaptan-covered silver gave the same peak position, whatever the chain length of the mercaptan. The 1357 and 1393 cm^{-1} peaks were probably those of PNBA adsorbed on flatter areas of the surface. On bare silver, the nitro band was composed of two peaks: the 1347 cm^{-1} peak gave one-third of the area and the 1357 cm^{-1} peak gave two-thirds. These intensity figures do not translate directly in numbers of adsorption sites, even assuming the same scattering efficiency for the two adsorbed species. First, the two types of adsorption sites may have two different SERS activity. Second, there is probably a nonlinear dependence of the Raman signal with surface coverage. In fact, we only can say that the very rough sites, which yield the 1347 cm^{-1} position, give one-third of the signal on bare silver.

Now, what is the origin of the observed shifts between the two adsorption sites? First, the shift was not a mere consequence of the change of environment of PNBA molecules. The 1347 and 1380 cm^{-1} positions existed for PNBA in the aliphatic layer as well as in the pure PNBA layer on bare silver. Second, the two positions for the nitro peak, and the two positions for the carboxylate peak, are not due to a purely electromagnetic phenomenon occurring in the course of the scattering process. With such a point of view, a shift in the peak position could be explained by the existence of different gradients of electromagnetic field strength at different adsorption sites.[3,22] Strong gradients should exist in the first 1−3 Å from the metal, and these gradients could make important the quadrupolar contribution of the field−molecule interaction. This could explain the shift of the carboxylate vibration, since this molecular group was near the silver. However, this cannot explain the shift of the nitro vibration, since this group was much farther from the surface. In fact, we think that the positions should be explained by the chemical interaction between PNBA and silver. The lower frequency for the symmetric stretching of the carboxylate, at 1380 cm^{-1}, may correspond to a slightly weaker C−O bond and thus to a slightly stronger CO_2−silver bond. At convex sites, silver atoms are more isolated, thus more able to participate in bonding. This affects the charge distribution within the PNBA molecule and also changes the frequency of the nitro symmetric stretch. Note that these two vibrations have the same symmetry in the molecule. The other nitro vibrations and the 1600 cm^{-1} vibration of the phenyl ring are much less affected. Alternatively, within the frame of the charge-transfer mechanism for SERS,[3] it may be possible to explain the shifts by a different charge transfer taking place at a rough, convex site. At such a site, the charge transfer would modify the frequency of the vibration at the same time as it creates an excited state responsible for the resonance effect. Thus, the observed shift is compatible with the fact that the adsorption sites are rough and convex.

Conclusion about the Use of SAM in Studies of Surface Chemistry

Surface-enhanced Raman spectra of *p*-nitrobenzoic acid chemisorbed onto silver island films showed two types of adsorption sites. When silver was previously coated with *n*-alkyl mercaptans, only one type of adsorption site was detected. The photoinduced reaction of PNBA on silver was hindered by the alkyl layer. The hexadecyl mercaptan layer, which did not prevent PNBA from chemisorbing on silver, did prevent the photoinduced reaction. These facts mean that, after coating, the available adsorption sites were isolated and situated on convex parts of the surface not well covered by alkyl mercaptans.

This paper shows the relevance of self-assembled monolayers (SAM) for the investigation of surface chemistry of a rough surface. They unveiled the specificity of different types of adsorption sites. SAM provided an easy way for the variation of the surface concentration of adsorbates. The chemisorption and photochemistry could be studied for very small densities of adsorbates, as well as isolated adsorbates. Other authors found several chemisorption sites on rough metallic surfaces by varying the surface concentration.[18] However, since they obtained this variation by simply exposing the surface to a variable amount of molecules, they could not know the location of the absorbates.

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