# ENHANCED RAMAN SCATTERING OF SILVER BENZENETHIOLATE

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A pellet of silver benzenethiolate shows strong surface-enhanced Raman scattering (SERS) after prolonged laser illumination. X-ray photoelectron spectroscopic and scanning electron microscopic studies show that the SERS activity arises via the photoformation of Ag islands on the pellet surface.

## 1. Introduction

Since its discovery by Fleischmann, Hendra and McQuillan [1], surface-enhanced Raman scattering (SERS) has been observed for molecules adsorbed on the surfaces of various metals such as Ag [2,3]. Au [4], Cu [5], In [6]. Strong SERS effects have been observed on surfaces with microscopic roughness. Surfaces such as electrochemically roughened electrodes [1], metal island films [7,8] and metal sols [9,10] are more effective than single crystals [11] for the observation of SERS. It has been suggested that surface roughness plays several important roles in SERS activity, the most important of which is to enhance the incident and scattered field intensities through surface plasmon resonance. This forms the basis for the electromagnetic interpretation ("EM theory") of the SERS phenomenon [12-14].

In SERS, a strong broad feature is often observed in the 1300–1600 cm<sup>-1</sup> region which is usually ascribed to graphite formed by the photodecomposition of organic materials near the surface [15–17]. According to the Auger electron spectroscopic study of Cooney and Mernagh [18], carbon was the dominating species on Ag electrode surfaces illuminated by the laser. Naked silver was barely present. From the fact that SERS became effective after laser illumination, it was proposed that the "photographitization" of organic compounds on the metal surface rather than the metal itself was responsible for the SERS phenomenon [18].

In a study on the SERS of benzenethiol on a silver surface, we recorded the ordinary Raman spectrum of silver benzenethiolate [19]. It was observed that the silver salt spectrum changed with time, eventually becoming identical to the SERS of benzenethiol. A detailed investigation on this system has been carried out, seeking information on the nature of the SERS phenomenon. The results are reported in this paper.

#### 2. Experimental

Silver benzenethiolate was prepared by mixing methanolic solutions of 1 M benzenethiol and 0.6 M silver nitrate in a 1:1 volume ratio [20,21]. The mixture was stirred vigorously during preparation. A pale yellow precipitate of silver benzenethiolate was readily produced in nearly 100% yield [22]. The precipitate was then filtered, rinsed thoroughly with methanol and water successively and dried under vacuum at 150°C. Pellets were made for Raman and infrared measurements.

The Raman spectra were obtained with a Japan Spectroscopic Company model R-300 laser Raman spectrophotometer using the 488 and 514.5 nm lines of an argon ion laser (Spectra Physics model 164-06) as the excitation source. Typical spectral slit widths used in the measurements were around  $10 \text{ cm}^{-1}$ . To

0 009-2614/89/\$ 03.50 © Elsevier Science Publishers B.V. (North-Holland Physics Publishing Division) obtain an ordinary Raman spectrum of the salt pellet, the pellet was spun at 3000 rpm to minimize laserinduced change and measurements were made within 3 min of the laser illumination [23]. The infrared spectrum was recorded with a Perkin-Elmer model 283 infrared spectrophotometer.

To prepare a SERS-active (see section 3) salt pellet, a pellet was illuminated using the 514.5 nm line of the laser with 0.2 W/cm<sup>2</sup> intensity for 3-4 h. An unfocused laser beam was used to provide nearly homogeneous intensity over the entire sample. X-ray photoelectron spectra of the pellets were obtained with a VSW Scientific Instruments XPS/Auger spectrometer. This was equipped with a 150 mm meanradius concentric hemispherical electron energy analyzer with a 16 gold-wire multichannel detection system, and the Mg K<sub>a</sub> line was used as a photon source for the XPS measurements. Samples were transferred into the analysis chamber (base pressure  $\leq 2 \times 10^{-9}$  Torr) by the fast entry air lock facility, and spectra were recorded as received without any cleaning procedure of the sample surface. Scanning electron micrographs for the pellets were obtained with a JEOL model JSM-35 SEM system.

The method of obtaining surface-enhanced Raman spectra in silver sols has been reported previously [24]. All the chemicals used were reagent grade. Triply distilled water was used for sample preparation.

## 3. Results and discussion

When a pellet of silver benzenethiolate salt was illuminated by the laser, it darkened quickly. Hence, it was necessary to lower the laser intensity and to rotate (3000 rpm) the pellet to obtain an ordinary Raman spectrum [23]. The Raman spectrum of silver benzenethiolate measured within 3 min of the laser illumination is reproduced in fig. 1a. The Raman spectrum of a darkened pellet obtained after a prolonged illumination is shown in fig. 1b. Even though the two spectra look similar, they differ in detail. Intensities of the corresponding minor peaks are substantially different in the two spectra. More importantly, the peak at 1079 cm<sup>-1</sup> in fig. 1a shifts to 1073 cm<sup>-1</sup> in fig. 1b. In our previous study on SERS of benzenethiol adsorbed on a silver surface



Fig. 1. (a) Ordinary Raman spectrum of silver benzenethiolatc measured within 3 min of laser illumination. Laser: 514.5 nm, 50 mW. (b) Ordinary Raman spectrum of silver benzenethiolate after prolonged laser illumination. Laser: 514.5 nm, 150 mW. (c) SERS spectrum of benzenethiol  $(5 \times 10^{-6} \text{ M})$  in silver sol. Laser: 514.5 nm, 120 mW. (d) Ordinary Raman spectrum of silver benzenethiolate covered with PNBA after prolonged laser illumination.  $\downarrow$  PNBA peaks. Laser: 514.5 nm, 100 mW.

[19], the red-shift of this peak from the position in the neat spectrum was taken as evidence indicating that benzenethiolate adsorbed via its sulfur atom. The Raman spectrum shown in fig. 1b is virtually the same as the SERS spectrum (fig. 1c) of benzenethiol in silver sols which was reported previously [19]. In addition, it is essentially the same as the SERS spectrum of this molecule adsorbed on an Ag film [23]. On the other hand, the infrared spectrum of the salt did not change with the laser illumination. Hence, it seems that a certain photoinduced process affects the surface properties of the pellet resulting in a Raman spectrum identical to the SERS spectrum. It is possible that the pellet surface has become SERS active by laser illumination, i.e. the spectrum in fig. 1b may be a genuine SERS spectrum. To check this possibility, minute amounts of a methanolic solution of p-nitrobenzoic acid (PNBA) was dropped onto the pellet surface such that the surface was covered with less than a monolayer of PNBA after solvent evaporation. The Raman spectrum of the salt pellet covered with PNBA is shown in fig. 1d. Overlapped by the strong benzenethiol peaks, the well-known SERS peaks of PNBA [25,26] appear at 864, 1108, 1343, 1377, 1598 cm<sup>-1</sup>, etc. with substantial intensities in this spectrum. Similar results have been obtained with several other adsorbates. These observations suggest that the pellet surface has become SERS-active following laser illumination. To gain information on the nature of the photoinduced process occurring on the pellet surface and to identify the SERSactive substrate, the pellet surface was analyzed further using XPS (X-ray photoelectron spectroscopy, ESCA) and SEM (scanning electron microscopy) techniques.

Low resolution XPS spectra obtained for the pellet with and without laser illumination are shown in figs. 2b and 2a, respectively. In the preparation of the laser illuminated pellet, efforts were made to darken the pellet surface homogeneously. A pellet which exhibited the Raman spectrum as shown in fig. 1b was chosen for the XPS analysis. Comparing the two XPS spectra, it can be concluded that laser-illumination did not cause a noticeable change in the elemental composition near the surface. Contrary to the observation by Cooney and Mernagh [18], the intensity of the carbon peak did not increase substantially relative to the Ag peak upon laser illumination. However, subtle changes in the XPS spectra can be seen in the high resolution spectra shown in fig. 3. In these spectra each of the Ag 3d core levels, namely Ag  $3d_{3/2}$  and  $3d_{5/2}$ , are split into two peaks. For example, the Ag  $3d_{5/2}$  component in the XPS spectrum (fig. 3a) of the unilluminated pellet consists of a major peak appearing at a binding energy of 376.2 eV and a weak shoulder at 373.8 eV. These binding



Fig. 2. Low-resolution X-ray photoelectron spectra of silver benzenethiolate (a) without and (b) with laser illumination for around 3-4 h. Vacuum condition: base pressure  $\leq 2 \times 10^{-9}$  Torr.



Fig. 3. Carbon 1s and silver 3d X-ray photoelectron spectra of silver benzenethiolate (a) without and (b) with laser illumination for around 3-4 h. Vacuum condition: base pressure  $\leq 2 \times 10^{-9}$  Torr.

energies are larger than quoted in the standard table [27] due to the uniform charging effect of the insulator sample. Considering that the binding energy increases with increasing oxidation number, the major and the minor peaks may be assigned to ionic and neutral Ag, respectively. One difficulty with such an assignment is the fact that the chemical shift difference between neutral and ionic (+1) silver [28] is usually smaller than the splitting shown in fig. 3. Nevertheless, the present anomaly may be attributed to the differences in charging effects for ionic and neutral Ag. Such a situation will certainly occur when ionic and neutral Ag are present in different domains on the surface, for example, when neutral Ag forms metallic clusters.

Based on the above interpretation, ionic silver dominates the surface of a pellet which was not illuminated by the laser. Immediately after the sample was inserted in the analysis chamber, the shoulder was hardly recognizable but became more noticeable as the XPS measurement went on. This neutral Ag peak is thought to have been generated by the X-ray itself or by stray light in the XPS chamber such as that emitted from the ionization gauge filament. Ag core levels appear as doublets in the XPS spectrum (fig. 3b) of the laser-illuminated pellet also. However, the components with smaller binding energy in each doublet are the major peaks in this case, contrary to the previous spectrum. Positions of the corresponding peaks in figs. 3a and 3b are slightly different probably due to the differences in surface charging effects in the measurements. The binding energies of the illuminated sample were corrected based on the C1s peak which appeared 0.5 eV higher in fig. 3b than in fig. 3a. The corrected peak positions are then in excellent agreement with those for the unilluminated sample. For example, the Ag  $3d_{5/2}$  doublet should appear in fig. 3b at 373.7 and 376.8 eV after correction corresponding to those at 373.8 and 376.2 eV, respectively, in fig. 3a. Hence,

it can be concluded that the majority of ionic Ag near the surface is converted to neutral form following laser illumination. We also note by comparing figs. 3a and 3b that the peak at lower binding energy is sharper than the peak at higher energy. This also supports our interpretation that the former peak comes from the metallic phase.

As mentioned previously, X-ray exposure of the unilluminated pellet in the course of the XPS measurement gradually changed the spectrum. After about 20 min of exposure, the XPS spectrum became almost identical to that of the laser-illuminated pellet. This indicates that X-rays as well as laser light produces neutral Ag through the photoreduction of ionic Ag. A similar observation has been reported for AgBr microcrystals which form the photographic latent image [29]. Hence, it seems that the laser induced process occurring on the pellet surface may be analogous to a photographic process. In fact, silverthiol complexes are sometimes used as spectral sensitizers in photography [30].



It was mentioned in section 1 that microscopic

Fig. 4. Scanning electron micrographs of silver benzenethiolate (a) without and (b) with laser illumination for around 3-4 h (magnification  $\times$  10000). The bar in (b) is 3.0  $\mu$ m. Laser: 514.5 nm, 150 mW.

roughness is needed on a metal surface to exhibit an efficient SERS effect [1,7-11]. For example, silver films composed of isolated islands of dimension 100-150 nm are known to be efficient SERS substrates [23,31]. To check the formation of microscopic Ag clusters on the pellet surface by laser illumination, scanning electron micrographs have been obtained. Scanning electron micrographs of the unilluminated and the laser-illuminated salt pellets are shown in figs. 4a and 4b, respectively. The appearance of islands is evident in fig. 4b. These islands are thought to be composed of Ag neutrals. Such an interpretation is consistent with the finding in the XPS spectrum that neutral Ag is physically separated from ionic Ag resulting in different charging effects. The diameters of the Ag islands in fig. 4b were around 100-140 nm. Hence, the size of the islands on pellets showing the optimum SERS effect is comparable to those on vapor-deposited [31] or chemically prepared Ag films [23].

The exact mechanism for the photoproduction of neutral Ag is a matter of conjecture. Absorption of a photon by the solid may induce homolytic cleavage resulting in neutral Ag. Alternatively, heterolytic cleavage of the Ag-S bond followed by photoreduction of Ag<sup>+</sup> may produce neutral Ag. Aggregation of the Ag atoms through diffusion will lead to the formation of islands. In an effort to obtain further information on the photoproduction of Ag islands, the kinetics of the increase of the SERS effect has been investigated by monitoring the intensity of the SERS peak at 1073 cm<sup>-1</sup> (fig. 1b). As mentioned previously, photoproduction of Ag islands is a complex process consisting of photoreduction of ionic Ag and diffusion. In addition, the dependence of surface enhancement on island size and shape [12,14,32] is not well understood. Certainly, one cannot expect a simple relation between the SERS enhancement factor and island size. An experimental kinetic curve for the increase in intensity of the 1073  $cm^{-1}$  peak is shown in fig. 5a. This curve was obtained by monitoring the 1073 cm<sup>-1</sup> peak using the 488 nm line of an argon ion laser with an intensity of  $\approx 6 \times 10^3$  W/ cm<sup>2</sup>. A semi-log plot derived from this curve is shown in fig. 5b. Here,  $I_0$  is the maximum intensity of the 1073 cm<sup>-1</sup> peak reached after prolonged laser irradiation. Considering the complexity of the process of island formation, the good linearity of the plot is sur-



Fig. 5. (a) Raman intensity versus time for the increase of the 1073 cm<sup>-1</sup> peak. (b) Ln  $[I_0-I(t)]$  versus time plot. See text. Laser: 488 nm, 80 mW.

prising. Despite the linearity however, the slope of the curve, i.e. the rate constant, displayed substantial scatter for different pellet samples. Moreover, linearity of the semi-log plot was not maintained when laser intensity was much lower or higher than the optimum value. When the laser intensity was much lower than the above, the time dependence of the Raman intensity adopted a sigmoid shape. Since the rate of photoproduction of neutral Ag is small with low laser intensity, a certain amount of time seems to be needed for the formation of Ag islands which are large enough to show strong SERS effects. Thus the rate of surface diffusion may play an important role in this case. When the laser intensity was very high, the SERS intensity grew rapidly and then decreased. The rapid increase of the SERS signal in the early stages of the laser illumination may be attributed to the synergic effect of the Ag islands. According to the electromagnetic theory of SERS, microscopic roughness on metal surfaces can increase the light intensity on the surface substantially [12,32,33]. Enhanced field intensities at the surface can then facilitate the photofragmentation of molecules adsorbed on the surface [34]. Enhanced photofragmentation on roughened metal surfaces such as Ag [35,36] and Cd [37] have been reported previously. Hence, rapid formation of Ag islands may quicken the photoproduction of neutral Ag even further. Eventually, photodissociation of benzenethiolate near the island may decrease the SERS intensity after prolonged irradiation.

In summary, a strong surface-enhanced Raman scattering was observed from silver benzenethiolate after prolonged laser illumination. From XPS and SEM studies, it was found that the photoformation of Ag islands on the pellet surface was responsible for the SERS. This observation could be important for a detailed understanding of photographic imaging phenomena.

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