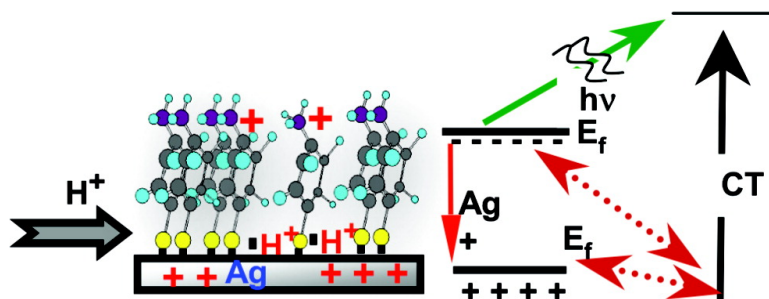


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Probing Silver Nanoparticles During Catalytic H₂ Evolution

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Abstract: Employing silver nanoparticles from a recently developed synthesis [Evanoff, D. D.; Chumanov, G. *J. Phys. Chem. B* **2004**, *108*, 13948] and a well-studied probe molecule, *p*-aminothiophenol, we follow changes at the surface of the particles during the conditioning and eventually the catalytic production of hydrogen from water using strongly reducing radicals. Injection of electrons into the particles causes pronounced variations in the intensity of the surface enhanced Raman scattering (SERS) spectrum of the probe molecule. These spectral changes are caused by changes in the Fermi-level energy that are in turn caused by changes in the silver ion concentrations or in the pH, or by changes in electron density in the particle. This correlation highlights the effect of the chemical potential on the SERS enhancement at the end of the particles synthesis. The intensity of the SERS spectra increases in the presence of the silver ions when excitation at 514 nm is utilized. When the Ag⁺ ions in the colloidal suspension are completely reduced by the radicals and the particles operate in the catalytic mode, the SERS spectrum is too weak to record, but it can reversibly be recovered upon the addition of Ag⁺. The effect of pH on the SERS intensity is similar in nature to that of the silver ions but is complicated by the pK_a of the aminothiols and the point of zero charge (pzc) of the particles. It is hypothesized that as the particles cross the pzc (around neutral pH) the electrostatic interaction between the protonated amine headgroup of the probe and the positively charged surface increases the density of probe molecules in the perpendicular orientation at the expense of a competing species. This conversion results in enhanced SERS signals and is observable during the preconditioning stage of the particles. Indeed, adsorption isotherms of the probe indicate the presence of two species. In analogous previous observations these two species have been attributed to perpendicular and flat adsorption orientations of the deprotonated probe molecule relative to the particle surface. However, preliminary density functional calculations on relevant prototypes raise the possibility that the two species may be the probe molecule and a cationic form produced by charge transfer in the ground state from the chemisorbed probe to the metal. These two forms of the probe have differing electronic structures and vibrational frequencies, with perhaps differing orientations relative to the surface. Whichever is the correct interpretation, a neutral molecule in a flat orientation or a radical cation, this species is easier to replace than the other in competitive adsorption by ethanethiol.

Introduction

Surface enhanced Raman scattering (SERS) was discovered more than three decades ago and has been widely utilized since then.¹ Yet, in spite of the immense sensitivity and detailed characterization potential that it provides, its utilization in providing insight into processes at metallic particle surfaces is rather limited. The lack of a universally accepted theoretical treatment of the enhancement mechanism, combined with experimental reproducibility issues, were major inhibitors to the widespread use of the technique in the catalysis arena, for instance. Nonetheless, the observation of single-molecule single-particle SERS spectra on silver particles^{2,3} rekindled interest in its applications and led to the intensive current use of SERS,

especially in sensing and characterization of biologically relevant molecules adsorbed on silver or gold substrates.⁴⁻⁷ In this report we explore the application of SERS to obtain information on silver particles during their operation as catalysts in the hydrogen evolution reaction. It is commonly believed that such a catalytic step will be necessary in any photochemical solar energy conversion scheme.⁸ The use of metallic particles to catalyze the conversion of one-electron-reducing radicals to molecular hydrogen is also well documented.⁹⁻¹¹ Henglein and co-workers

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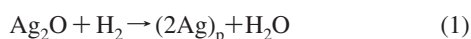
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outlined the mechanism for these catalytic reactions as a sequence of electron-transfer followed by proton-transfer steps, essentially an electrochemical sequence,¹² but the intimate details of these steps remain unclear. We address these details in the present report using a sensitive SERS-active probe molecule at the surface of silver nanoparticles.

Most common procedures to synthesize silver particles utilize organic molecules, either as reductants or as stabilizers and often both. A common molecule useful in SERS studies is citrate, which reduces the silver ion precursor and acts as a particle stabilizer as well.¹³ Because of concerns regarding competing adsorption, and more importantly participation in the catalysis by these organic foreign molecules, we did not use these particles in the context of redox catalysis.¹⁴ Indeed, recent observations by Redmond et al. confirm these concerns and suggest efficient photochemical reaction between the stabilizer and the metallic particles upon excitation.^{15,16} On the other hand, we were attracted to the recently reported synthesis of Evanoff and Chumanov because it produces particles that contain no foreign component other than only silver or water and their ions (reaction 1).^{17,18}



In an earlier study we outlined our understanding of the mechanism of production of the particles and the source of their unusual stability, which stems from the presence of hydroxide ions at the surface.¹⁹ Thus, the hydrophobic character of a metallic surface is transformed into an oxide-like hydrophilic surface that allows accumulation of very high concentrations of the metallic particles. Furthermore, as Evanoff and Chumanov already emphasized in their original description of this system,¹⁷ we find the flexibility that it provides in choice of size and in simplicity of speciation very useful. On the other hand, we recognized in our earlier report the impact of the rather high, residual concentration of silver ions.¹⁹ This is simply a result of the relatively high redox potential of the H^+/H_2 couple. A stronger reductant, for example radiolytically produced radicals in our case, is required before any redox catalysis to produce H_2 takes place. The changes that occur during this “preconditioning” stage of the particles, prior to the start of the redox catalysis, lead to significant changes in the SERS spectra and intensity of the probe utilized here.

We chose *p*-aminothiophenol (*p*-ATP) as a convenient probe. This thoroughly studied molecule, like most other thiols, forms a monolayer on the surface of silver; its SERS activity is well documented and has been studied by many groups.^{20–30} Assignment of the vibrational bands by Osawa et al. is commonly accepted, and the evidence for the contribution of a charge-transfer band to the surface enhancement seems convincing.²¹ Furthermore, Osawa et al. have shown that the contribution of this so-called chemical enhancement is sensitive to the potential of the enhancing surface. We make use of the sensitivity of enhancement to the energy of the Fermi level in interpreting

our present observations. We find that the probe provides meaningful information on the state of the particles (and the probe as well) during catalytic hydrogen evolution from water reduction. In particular the probe reports major changes at the particle surface during the preconditioning stage when the overpotential on the particles increasingly becomes more negative prior to the start of the catalysis itself. Whereas the probe does not undergo serious chemical degradation during the catalysis, significant SERS intensity changes are observed. These are discussed in the context of the changes that occur in orientation and/or electronic distribution between the particle and the probe molecule. Density functional theory calculations on the impact of redistribution of electronic charge between the molecule and the metallic substrate highlight the possibility of formation of radical species upon adsorption. However, detailed description of the changes in the *p*-ATP probe molecule is still under scrutiny.

Experimental Section

Chemicals. Ag_2O powder (99.99% from Alfa Aesar, 150 μm particle size), acetone and 2-propanol (ACS certified from Fisher Scientific), *p*-aminothiophenol and AgClO_4 (both from Aldrich) were used as received. Hydrogen and argon gases of the highest purity were from Mittler Inc. Deionized ultrapure water from a Millipure Milli-Q system was used throughout this study.

Silver Particles Synthesis and Characterization. “Naked” silver colloid dispersions free of any foreign stabilizer were prepared following the method of Evanoff and Chumanov according to equation 1. Briefly, a 5-L Pyrex round-bottom three-necked flask equipped with a thermometer, a reverse condenser, and a spout for drawing samples was used for the synthesis. Each synthesis followed the same basic procedure: the flask was filled with 3.0 L of deionized water and 2.5–3.0 g of Ag_2O powder, and its temperature was raised to 70 °C. Following equilibration for an hour the vessel was flushed for 10 min and then pressurized with H_2 to 1.7 atm to initiate the reaction. During the reaction, aliquots (100–120 mL) of the reaction mixture were taken through the spout at regular intervals. A fine glass frit at the bottom of the spout blocks the transfer of solid Ag_2O particles into the samples. These were used in the characterization of the particles of various sizes, as well as in the study of the H_2 evolution process. Progress of the reduction was monitored by measuring the UV–vis extinction spectra of samples withdrawn from the reaction vessel and cooled to room temperature on a Varian Cary 50-Bio spectrophotometer. All the spectra shown here are normalized to 1 cm optical path. When the needed estimated-largest particle size was obtained the excess H_2 pressure was released, and the temperature dropped to the ambient. All following speciation measurements were conducted after cooling to room temperature.

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Total silver concentration was measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on an Optima 3300 XL Perkin-Elmer spectrometer, after complete dissolution of the particles in concentrated nitric acid. Conductivity measurements were done using a Chemtrix type 70 conductivity meter. Higher concentrations than those obtained directly from the as-synthesized original suspensions were obtained by decanting the nearly clear supernatant solution when the particles were settled to the bottom of the flask. It was verified that this procedure does not affect size of particles or their distribution. The pH was adjusted using NaOH or HClO₄. Particle size and size distribution was routinely measured using dynamic light scattering (DLS) using a Beckman-Coulter N4 Plus instrument. To verify size determination a few samples were also examined under JEOL-1000SX transmission electron microscope (TEM). Further characterizations of the silver suspensions followed the procedures reported in our previous work or as detailed below.^{19,31}

Raman Microscopy. Raman and SERS spectra were collected with a Renishaw RM1000 Raman spectrometer equipped with CCD detector, and a confocal Leica microscope. The spectrograph uses 1200 g/mm gratings and a linearly polarized argon-ion excitation laser (514.5 nm) operating at 1–10 mW power. Each spectrum was collected for approximately 5–7 min. Spectral shift calibration was repeatedly checked using the Raman lines for ethanol. All samples for SERS measurements were prepared by adding 10–100 μ L of freshly prepared *p*-ATP stock solution in 2-propanol. Unless otherwise specified, the concentration of *p*-ATP in the silver nanoparticles solution was 1.0 μ M. Again, unless stated otherwise, irradiated samples were degassed by bubbling argon prior to collection of the SERS spectra, as well as before the irradiation. All spectra (and irradiations for SERS measurements) were collected in cylindrical, 1.0 cm diameter, septum-capped cuvettes containing the Ar-bubbled solutions. Following the irradiation the Ag suspensions were again bubbled with argon (or air or H₂ when specified) prior to the measurements. Baselines for all spectra were corrected for Rayleigh scattering and for fluorescence from monophotonic excitation of the suspensions. This procedure also removes minor contributions from direct Raman scattering by the high 2-propanol concentrations.

The ultrahigh sensitivity of SERS is a cause of concern in the present study of relative band intensities. In particular, the potential for hot spots or junctions may skew the observations.^{33,43} To minimize the impact of these random events a large number of particles was covered in the laser cross section of all experiments, low laser power was used, and each sequence of measurements was repeated at least three times.

Irradiation. Irradiation of the samples was performed with a JL Shepherd & Assoc. model 109-68 ⁶⁰Co γ -source at a dose rate of 75 \pm 5 Gy/min as determined by the Fricke dosimeter in the same cells used for the H₂ and Raman measurements. For monitoring H₂ yields, an inline gas chromatograph (Varian ChromPack CP-3800) was connected to a well-regulated Argon gas stream that continuously bubbled through the sample cell made of a 1 \times 1 \times 3 cm quartz cuvette. A four-way valve allowed the cell to be isolated from the Ar stream during the course of the radiolysis. Opening the valve directed the accumulated volatile products into a 3-m molecular-sieve 5 \AA chromatographic column held at 50 $^{\circ}$ C. Products were measured with a thermal-conductivity detector. A septum for the injection of calibration gases was placed upstream from the sample cell. Gas flow through the sample was maintained at 40 cm³ min⁻¹. Further details of the gas chromatography procedure are described elsewhere.^{19,31} All irradiated solutions contained 0.1 M acetone and 1.0 M 2-propanol. Under

these conditions the only radiolytically produced relevant radicals are the (CH₃)₂COH radicals, which recombine in the absence of the silver particles but produce molecular hydrogen from water when the catalytic process dominates.¹⁹ Samples for SERS measurements were irradiated in a cylindrical cuvette at the same dose rate as the samples for H₂ evolution. For SERS measurements each sample was irradiated only once for the dose shown. On the other hand, for H₂ yield determination the same sample was irradiated repeatedly, but yields were calculated for the last absorbed dose.

It is now well established that, in the solutions used here, the radiation generates within a few microseconds primarily a single reducing radical, (CH₃)₂COH. These radicals can be converted entirely to H₂ via the catalytic reaction of the silver particles, provided the overpotential required for hydrogen evolution is attained. The maximum H₂ yield that can be obtained is \sim 0.42 μ mol J⁻¹, of which 0.11 μ mol J⁻¹ is from the direct radiolysis of water and the remaining is from the catalytic reaction of the radicals with the particles. This high yield can be modified by competing reactions of the radicals ranging from radical–radical reactions to catalytic reduction of H₂O₂, also produced in water radiolysis.¹⁹ Because of the relatively high silver and 2-propanol concentrations used in the present study the high limiting yield is achieved once all Ag⁺ is consumed in a preconditioning stage.

Electronic Structure Calculations. To gain insight into the interactions of *p*-ATP with silver we conducted preliminary calculations on the structures and changes in vibrational spectra for prototypes of the various potentially relevant species at the surface. Detailed analysis of the calculations is beyond the scope of this report, but even preliminary results from the computational analysis do highlight a significant effect of charge redistribution between the metallic substrate and the molecule on the vibrational modes. Calculations were made on the parent *p*-ATP compound H₂N-Ph-SH, the analog H₂N-Ph-SAg formed by replacing the thiol proton with a single silver ion, the radical cation H₂N-Ph-SAg⁺ and the corresponding N-protonated species, ⁺H₃N-Ph-SAg and ⁺H₃N-Ph-SAg⁺. In addition, several of the acid–base forms of the molecule and the radical were calculated but will not be discussed other than to note that they generally corroborate the findings presented here. The PW91PW91 gradient-corrected density functional³² was used together with an “ultrafine” integration grid that is a pruned version of a grid having 99 radial shells and 590 angular points per shell about each atom. The basis set consisted of the 6-31+G* basis^{34,35} for first and second-row atoms and the LANL2DZ basis³⁶ for silver that uses an effective core potential to replace 28 core electrons, leaving 19 valence electrons to be explicitly treated for each silver atom. All calculations were carried out with the Gaussian03 program.³⁷

It has been recommended in the literature³⁸ that, in order to compare favorably with experimentally observed vibrational frequencies of small organic molecules, the harmonic frequencies obtained from methods closely related to PW91PW91/6-31+G* should be empirically scaled by a factor of approximately 0.95. However, we found that with benzene the PW91PW91/6-31+G* harmonic frequencies should instead be scaled by a factor of about 1.08 to obtain the best overall mean square agreement with experiment. In light of these disparate findings, the frequencies reported here are not scaled at all.

Results and Discussion

Synthesis and Characterization of the Particles. Our earlier work provides guidelines for choice of the synthetic conditions

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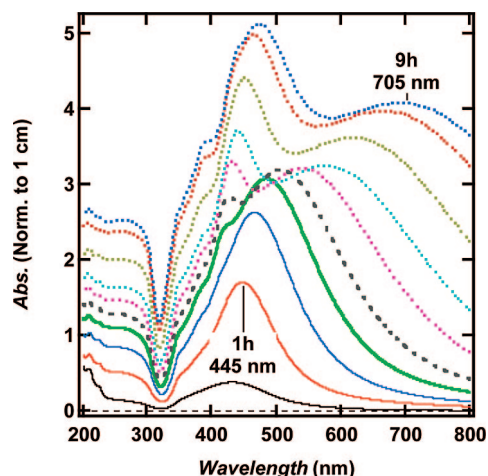
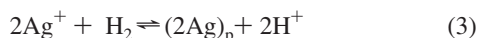
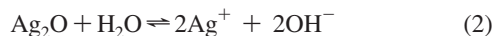


Figure 1. Spectral evolution of the growing particles taken at 1 h intervals (except the lowest spectrum, which was measured 15 min after initiation of the reaction).

for particles of the preferred sizes. In the present study we aimed at collecting larger particles in the range of 50–200 nm in diameter. As was already discussed the net reaction 1 can be described as a sequence of consecutive reactions, dissolution of the oxide to generate mostly Ag^+ ions (with negligible contribution from $\text{Ag}(\text{OH})_2^-$ at the pH's studied here, 9–10) and reduction of the silver ions by hydrogen, reactions 2 and 3, respectively.



The relative rates of these two processes determine the steady-state concentration of Ag^+ and the pH during the synthesis and, thereby, the size of the particles. In our experience when the solution is undisturbed during the synthesis, a thin coating of reduced silver accumulates on the large Ag_2O particles, which remain at the bottom of the vessel. This inhibits their further dissolution, and the steady state concentration of Ag^+ ions during the synthesis continuously decreases. Under these conditions much of the reaction occurs while increasing seed concentrations, and the size obtained is essentially constant at ~ 30 nm. In the present experiments we gently stirred the solutions during the synthesis. The rate of Ag_2O dissolution is then relatively fast, and the rate-determining step is the reduction reaction. This leads to a nearly constant concentration of the seeds, but their size continuously increases. This is clearly evident from the spectral evolution shown in Figure 1, by TEM and DLS measurements, and is also supported by the speciation described below. Chumanov and co-workers gave complete spectroscopic analysis of the extinction spectra of the particles observed during the growth process.³⁹ The lowest energy-band is the plasmon dipole, and the higher multipole bands can be seen progressively at higher energies. The sharp bands observed in Figure 1 in the vicinity of 210 nm are from residual Ag^+ ions. The correlation between the size of the particles and the wavelength of maximum extinction of the dipole-plasmon mode is shown in the top of Figure 2.

The concentration of silver ions in the bulk of the solution in the course of the reaction was determined from conductivity

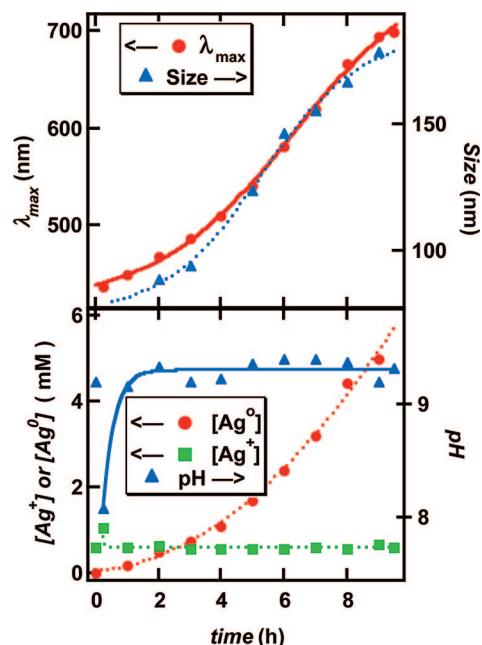


Figure 2. Changes in wavelength of maximum extinction of the dipole component (top, left-hand side scale [LHS]), size (top, RHS scale), pH (bottom, RHS, triangles), metallic Ag concentration (bottom, LHS, red circles), and $[\text{Ag}^+]$ (bottom, LHS, green squares) of the preparation of Figure 1.

and pH measurements, assuming that OH^- and Ag^+ are the only ions in the solution. The limiting molar conductivities of these two ions were taken to be 197.8 and 61.9 $\text{S cm}^2 \text{mol}^{-1}$, respectively. The solution pH equilibrates at 9.3 prior to the reduction (reaction 2) as the oxide dissolves, since the concentration of the hydroxide, $\text{Ag}(\text{OH})_2^-$, is negligible. As Figure 2 shows, initiation of the reduction (reaction 3) leads to a decrease in the pH (to around pH 8.4) and concomitantly to a decrease in free Ag^+ ion concentration. However, the pH recovers to ~ 9.3 , and a steady state of $[\text{Ag}^+] = 5.6 \times 10^{-4}$ M, close to the solubility of Ag^+ at this pH, is reestablished within the first hour of the reaction. Both the pH and $[\text{Ag}^+]$ are then maintained nearly constant throughout the synthesis in this experiment. This pH is above the point-of-zero-charge (pzc) of the particles, and they are then stabilized by hydroxide ions that provide the electrostatic stabilization and a hydrophilic surface.

In a third speciation experiment we also determined the total silver, ions and metallic, using ICP following dissolution of the particles in concentrated nitric acid. Results from these experiments are also given in Figure 2. As Figure 2 shows, the concentration of ions exceeds that of the metallic silver for nearly 2 h during the synthesis. Beyond 2 h the concentration of metallic silver is higher than that of the ions, but the latter remains constant as the total silver concentration increases. By definition then, the redox potential of the Ag^+/Ag^0 couple remains constant. This method of speciation was utilized across the present study with essentially the same quantitative observations. Unless otherwise stated, the results described below were collected from the largest particles shown in Figure 2.

Preliminary SERS Observations. All of the particles of the various sizes synthesized here show strong enhancement of the Raman lines of *p*-ATP that are commonly seen on silver (Figure 3, top).²¹ Relative line intensities were measured for the particles of the various sizes, but meaningful comparison is complicated by the many factors other than size that affect the

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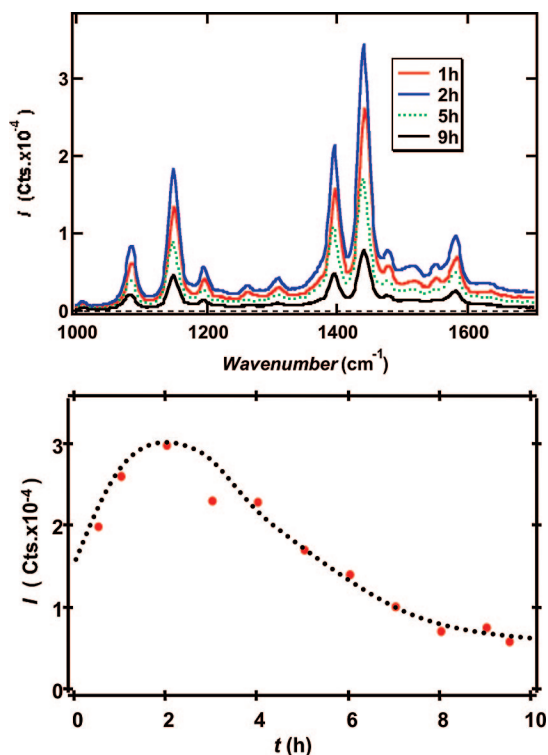


Figure 3. SERS spectra of 1×10^{-6} M *p*-ATP on the silver nanoparticles (top) and the intensity of the 1440 cm^{-1} band (bottom) at various times after start of the preparation. Solutions contain 1 M 2-propanol and 0.1 M acetone at pH 9.3. All solutions were adjusted to absorbance of 0.85 in 1 cm cells at 514 nm.

intensity of the Raman signals.⁴⁰ Some of these effects are discussed below. Therefore, Figure 3 displays the SERS spectra of the various samples withdrawn from the same preparation of Figure 2 and at the same time intervals. They are shown as a function of synthesis time and not as a function of size to eliminate the implication that size is the dominant parameter. Nonetheless, it is also clear that the size of the particles increases with reaction time. For the spectra of Figure 3, concentrations of the suspensions were adjusted (maintaining pH 9.3) to give absorbance of 0.85 ± 0.05 in 1 cm optical-path cells at the excitation wavelength of 514 nm. The relative intensities of the various bands remain the same throughout the reaction within the accuracy of the measured intensities.

The dependence of SERS signal intensities on concentration of *p*-ATP was measured for the largest particles of Figure 2 (9 h synthesis). Adsorption isotherms constructed from the intensities of the bands at 1440 and 1520 cm^{-1} are shown in Figure 4a. The spectra in the fingerprint region of 1300–1600 cm^{-1} at low and high *p*-ATP concentrations are also shown in Figure 4. The band at 1520 cm^{-1} saturates at significantly lower concentrations than the 1440 cm^{-1} band. The difference in behavior of these two bands is a recurring and not completely understood observation across this study. Following the assignment of Osawa et al.²¹ and the later interpretation of Formm et al.⁴¹ the 1440 cm^{-1} band is one of the four strong b_2 symmetry-species in-plane benzene-like modes in the approximate C_{2v} symmetry of the ring segments of *p*-ATP molecules adsorbed

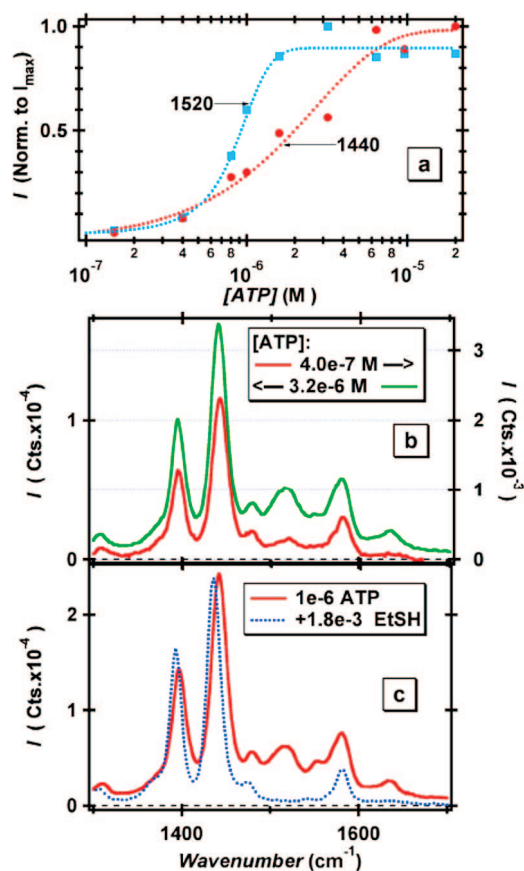


Figure 4. (a) Intensity of the 1440 cm^{-1} and 1520 cm^{-1} bands vs $[p\text{-ATP}]$ at $[\text{Ag}]_p = 5 \times 10^{-3}$ M (9 h in Figure 2). Intensities of both were normalized to their corresponding highest intensity. (b) Fingerprint-region spectra at low and high *p*-ATP concentrations. Note that the right-hand side axis is 20× more sensitive than the LHS axis. (c) Effect of ethanethiol on the spectrum of *p*-ATP.

standing perpendicular relative to the surface. The higher energy mode, observed around 1500–1550 cm^{-1} , shows weaker enhancement. Osawa et al.²¹ observe no mode at all in this region. Following the suggestion of Formm et al.⁴¹ in a similar situation, this may indicate a vibration that is present in the neutral molecule but is enhanced only upon adsorption of some of the molecules in a flat orientation relative to the surface, wherein a different pattern of mode enhancements would be obtained. Within this framework one would conclude, then, that the molecule in a flat orientation saturates before the perpendicular one, presumably due to the larger effective cross section required for the flat orientation. Another possibility is suggested by our preliminary calculations, which indicate that the spectral region around 1520 cm^{-1} is highly sensitive to charge redistribution between the molecule and the particle. This distribution is bound to depend on surface coverage. This issue is discussed further below. Regardless of the exact origin of the band around 1520 cm^{-1} , the corresponding molecular species that gives rise to it is easier to exchange than the one that gives rise to the 1440 cm^{-1} band.

Because of the very low solubility of *p*-ATP at the pH's used, and in line with most other aromatic thiols, it is assumed that *p*-ATP is completely adsorbed at all of the concentrations used in Figure 4. From the concentration of metallic Ag, the particle size (5×10^{-3} M and 178 nm respectively, Figure 2), and the concentration of *p*-ATP when saturation is achieved (5.8×10^{-6} M for both orientations combined, Figure 4a), one calculates

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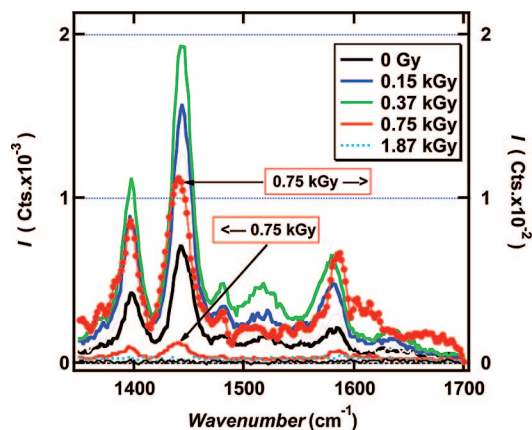


Figure 5. Effect of radiation dose on SERS spectra. All spectra are plotted on the LHS scale. The spectrum after 0.75 kGy (red) is also shown on the $10\times$ more sensitive scale of the RHS to emphasize changes in relative intensities.

an effective footprint cross-section of 0.5 nm^2 per *p*-ATP molecule on the particles. Similar cross sections were observed for other molecules on various particles.⁴² The relatively small cross section indicates monolayer formation dominated by perpendicular adsorption relative to the surface. Because of the low enhancement of the 1520 cm^{-1} band, and the unclear origin of that band, the fraction of probe molecules in each situation is difficult to estimate. Regardless, the 1440 cm^{-1} band is less sensitive than the 1520 cm^{-1} band to the presence of other adsorbates, suggesting weaker adsorption for the latter species. Upon the addition of ethanethiol (EtSH) at a constant pH of 9.3 both bands initially decrease, indicating exchange of *p*-ATP by EtSH. However, at $[\text{EtSH}] > 5 \times 10^{-4} \text{ M}$ the 1520 cm^{-1} band completely disappears, while the 1440 cm^{-1} actually increases back to the initial intensity (Figure 4c). This increase of one band at the expense of another indicates interconversion from one species to another, with a stronger enhanced mode. Again, changes in orientation from perpendicular to flat and/or in charge distribution can be invoked to rationalize this behavior (*vide infra*). All the following experiments were conducted with $1 \times 10^{-6} \text{ M}$ *p*-ATP (30% and 60% saturation for the 1440 and 1520 cm^{-1} , respectively).

SERS Following Irradiation. The SERS spectra and intensity of the various *p*-ATP bands were measured following increasing doses of absorbed irradiation. An example of the spectra collected at various doses is shown in Figure 5. The intensity of the enhanced bands increases initially and then declines precipitously. For example, in Figure 5 the intensity of the 1440 cm^{-1} band increases as the absorbed dose increases up to 370 Gy and then declines essentially to the baseline. Note that at the dose rate used here (75 Gy/min) approximately $5 \times 10^{-5} \text{ M}$ of reducing equivalents are generated in a minute. This initial increase followed by decrease of intensity has been observed in a large number of independently prepared samples, but the dose at which the intensity enhancement reverses its direction depends on the initial concentrations of silver particles, Ag^+ ions, and the pH. These effects correlate with the fraction of radiolytically generated reducing radicals that react with the particles. Radicals that react via other pathways do not affect the signal intensity. Irradiation with over 1 kGy had only small effect on the signal at low particle concentration indicating that

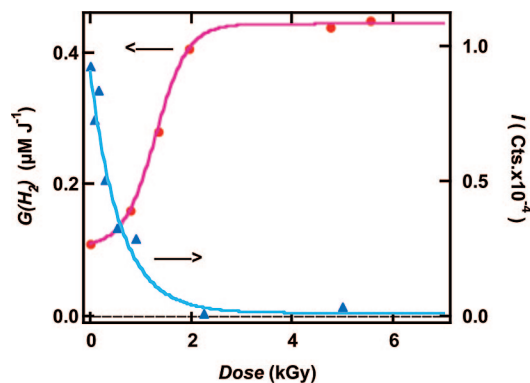


Figure 6. Yield of H_2 (red circle; LHS) and intensity of the 1440 cm^{-1} SERS line (blue triangle; RHS) as a function of dose absorbed by the particle suspension. Solution contains: $[\text{Ag}]_p = 2.7 \times 10^{-2} \text{ M}$, $[\text{Ag}^+] = 5.6 \times 10^{-3} \text{ M}$, pH 9.3 and the other components are as in Figure 3.

generation of various products in the aqueous phase does not affect the SERS spectra. Furthermore, as is emphasized in Figure 5, the relative intensities of the bands change at the higher doses, similar to the observation of Figure 4c. Notably, the band at around 1520 cm^{-1} becomes much weaker relative to the 1440 and 1580 cm^{-1} bands at high doses.

We first address the diminishing intensity at high doses. Figure 6 correlates the decreasing SERS band intensities with the measured H_2 yields following various irradiation doses. A similar correlation was reproduced in many repeated experiments on independently synthesized particles. On the scale of doses shown in Figure 6 the region of increased SERS intensity is too short to display. One concludes that the reduction in SERS intensity, particularly of the strongest enhanced bands, occurs during the preconditioning stage. Furthermore, it again correlates with the extent of the radical reaction with the particles. When the concentration of the particles is low, the fraction of radicals that reacts with the particles decreases. Under these conditions then, higher doses are required to completely reduce Ag^+ (reaction 4) and concurrently, to extinguish the SERS signal and obtain maximum catalytic activity.



The decrease in the SERS intensities is not a result of destruction of either *p*-ATP or the particles. Addition of the probe molecules after the irradiation leads to the same result as their addition before the start of the irradiation. At the end of the irradiation no significant amount of any radiation product can accumulate. The radiolytically initiated reactions primarily convert 2-propanol to acetone, and perhaps produce low concentrations of recombination products from the radicals. Hydrogen peroxide from the radiolysis of water is reduced to water. As mentioned above, direct reactions of the radicals with the particles are required in order to bring about the decrease in intensity. Therefore, the diminished SERS activity is not due to some radiolytic degradation of *p*-ATP. Most convincing, the SERS spectra of *p*-ATP can be restored by addition of Ag^+ ions to the suspensions after the irradiation, regardless of whether *p*-ATP was added before or after the irradiation. Figure 7 shows the effect of silver ions on the intensity of the bands in the 1400 cm^{-1} region. Following irradiation with a dose of 4.6 kGy the SERS spectrum of *p*-ATP is completely quenched. On addition of $1.8 \times 10^{-4} \text{ M}$ Ag^+ to the suspension the spectrum is restored. The SERS intensity was similar then to that obtained before the irradiation. This effect is specific to

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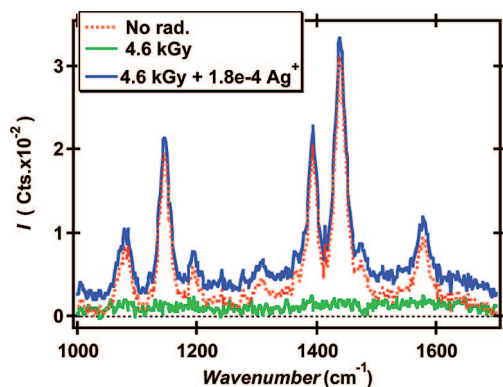


Figure 7. Effect of Ag⁺ ions on SERS spectrum following the irradiation. Dotted red spectrum: no radiation. Green spectrum: following a dose of 4.6 kGy. Blue spectrum: following addition of 1.8×10^{-4} M Ag⁺ after the irradiation.

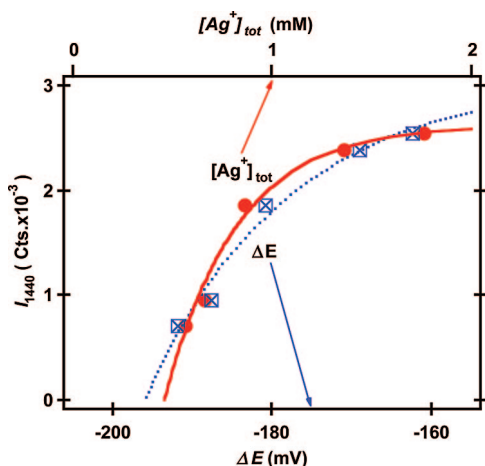


Figure 8. Effect of [Ag⁺] (red dots; top scale) and the corresponding change in Ag⁺/Ag⁰ redox potential (blue squares; bottom scale) on the intensity of the 1440 cm⁻¹ line. [Ag⁺]_{tot} includes initial and added ions.

Ag⁺. It has been previously observed⁴³ and verified here that Na⁺ or K⁺ ions have essentially no effect on the SERS intensity.

Effect of Ag⁺. The result described above suggests that [Ag⁺] ions affect the intensity of the spectra. Therefore, the SERS intensity as a function of added silver ions (no irradiation) was examined. Indeed the intensity of the spectrum increases with increasing [Ag⁺] at least to 2×10^{-3} M Ag⁺ with little change in the relative intensity of the various bands. Above this concentration, the integrity of the particles deteriorates due to the increased ionic strength. The effect of [Ag⁺] on the SERS intensity is attributed to the dependence of the redox potential of the Ag⁺/Ag⁰ couple, and thus to the energy of the Fermi level of the particles on the concentrations. Figure 8 demonstrates this dependence both in terms of Ag⁺ concentration and the corresponding change in the redox potential. The sensitivity of the SERS spectra to the Fermi-level energy (and the electrode potential) has been attributed by Osawa et al. to vibrational coupling of the ground state of the molecule and its charge-transfer state at the laser excitation via the Fermi level.²¹ As in resonance enhancement then, shifting the Fermi level borrows more or less intensity from the ground state, depending on the energy of the Fermi level and excitation light. In the present case, the redox potential of the Ag⁺/Ag⁰ couple is determined by the concentration of the silver ions via a Nernst term. Figure 8 demonstrates this change in Fermi-level energy when [Ag⁺]

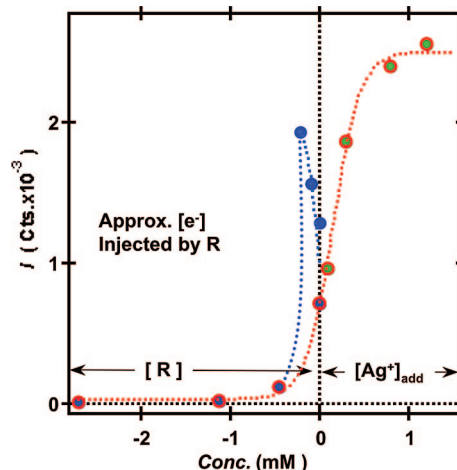


Figure 9. Intensity of the *p*-ATP SERS band at 1440 cm⁻¹ vs added [Ag⁺] (positive concentration range) or approximate concentration of electrons injected into the particles from radiolytically generated radicals, R (negative concentration range). Some of these electrons do not remain on the particle since they generate H₂ (see text).

was changed in the accessible range. From the dependence of intensity on electrode potential given by Osawa et al.²¹ using a similar excitation laser to the one used here, we estimate that the particles are positioned at ~ -0.1 V vs NHE at the highest Ag⁺ shown in Figure 8. On the other hand, during the catalytic H₂ evolution reaction the SERS spectrum vanishes. The same correlation then implies that the overpotential on the particles is more negative than -0.45 V vs NHE. In the following we turn to the increase in signal intensity at low doses.

Effect of pH on SERS. The effect of radiation dose on the SERS-spectra intensity during the preconditioning stage could perhaps have been attributed to the rising Fermi level except that the pH must change as well if silver ions are reduced since electroneutrality must be maintained (reaction 4). Under these conditions, as is often observed for oxide interfaces, the reduction of silver ions should be compensated by neutralization of oxide ions at the interface and the Fermi level is expected to remain essentially unchanged. Yet, the observation of increased SERS signal followed by declining intensity indicates that the effect of pH is more complicated than this simple description.

The increase in SERS signal during the early stages of the irradiation is shown in Figure 9 at the negative side of the concentration axis for a set of experiments on the same suspension as that of Figure 8. To maintain the same units the dose absorbed by the sample was converted to concentration of radicals in that figure. When all radicals react with the particles to reduce Ag⁺ this side of the axis displays reduction in residual [Ag⁺] from its initial concentration. However, it is clear from Figure 6 that an increasing fraction of the radicals generates H₂ during the preconditioning stage, and therefore, not all electrons that were transferred to the particle remain there. We did not attempt to correct for this fraction in the presentation of Figure 9.

To explore the effect of pH we added acid (HClO₄) and base (NaOH) to the “as-synthesized” suspensions. These experiments are limited by the effect of ionic strength on the stability of the suspension at both acid and base extremes (pH 11 and pH 2.8), and by the instability of the particles near the pzc. Nonetheless, in the range of pH 11 to 8.2 and 4 to 2.5 the suspensions were stable for a few hours allowing reliable SERS spectra collection. Figure 10 depicts the intensity of several of the more prominent

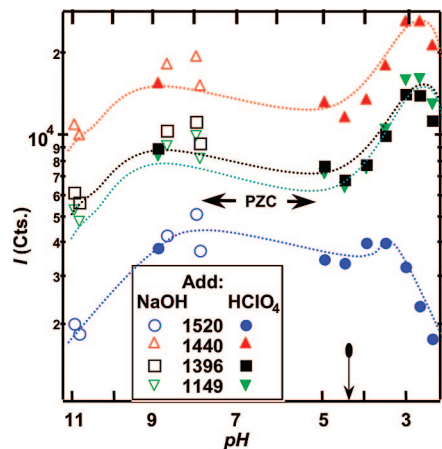


Figure 10. Effect of pH on the SERS intensity of several bands. (Filled symbols) Addition of HClO_4 ; (open symbols) addition of NaOH . The region around the pzc, indicated by a double arrow, is inaccessible. The arrow at the bottom indicates the calculated $[\text{H}^+]$ radiolytically generated after 1 min irradiation when all the radicals transfer an electron to the particles but H_2 does not evolve yet. Note the decrease in intensity of the 1520 cm^{-1} band at $\text{pH } 4\text{--}3$ while the other bands increase.

bands, as well as the 1520 cm^{-1} band, over the full range of accessible pH. As the pH decreases from 11 to ~ 8 the intensity increases, and for most bands this trend continues to $\text{pH } \sim 3$. However, the intensity of the 1520 cm^{-1} band decreases in the range of $\text{pH } 4\text{--}3$ while the intensities of the other bands continue to increase. As the pH crosses to the acidic side the concomitant increase of positive charge at the particle surface is accompanied by protonation of the amine terminus of *p*-ATP. However, it may also be accompanied by charge transfer between *p*-ATP and the particles, similar to the effect of Ag^+ or addition of EtSH. On further increase in acidity ($\text{pH} < 3$) the thiolate headgroup also protonates, *p*-ATP molecules desorb from the surface, and the SERS intensity decreases across the whole spectrum.

Charge Redistribution. Changes of relative intensities at the band in the $1500\text{--}1550\text{ cm}^{-1}$ range indicate the presence of more than a single species. Osawa et al.²¹ report no band in this range, and Fromm et al.⁴¹ suggest changes in adsorption orientation as the cause for similar changes in enhancements. Calculations, though, raise the possibility that charge transfer between silver and the molecule in the ground state may provide an alternative explanation of the observed changes in the vibrational spectra. Table 1 summarizes those vibrational frequencies calculated to lie in the $1400\text{--}1650\text{ cm}^{-1}$ range for a few species that model those which might be present in this

system. The species include the parent molecule ($\text{H}_2\text{N-Ph-SH}$), the silver salt and its radical-cation ($\text{H}_2\text{N-Ph-SAg}$ and $\text{H}_2\text{N-Ph-SAg}^+$, respectively), and the amine-protonated salt and its radical cation ($^+\text{H}_3\text{N-Ph-SAg}$ and $^+\text{H}_3\text{N-Ph-SAg}^+$, respectively), chosen to emphasize the effects of charge redistribution between the probe and the particle. Figure 11 shows the corresponding optimized structures of these species. For the parent molecule, agreement with Osawa's et al.²¹ experimentally observed vibrational frequencies and assignments is very good. Removal of an electron from the molecule or from its amine-protonated analog leads to a pronounced downshift in the frequency of the 8b mode, bringing it into the $\sim 1500\text{--}1550\text{ cm}^{-1}$ region and so providing an alternative explanation for the strongly enhanced SERS spectrum observed in this region. On the other hand, the 1440 cm^{-1} band experiences much smaller shifts on moving from the molecules to the radicals. Changes in charge distribution upon adsorption on silver that lead to vibrational frequencies that resemble those of the radical rather than the molecule have been reported for several cases.^{44,45} Mulliken charge populations are also shown in Table 1. While the absolute charges may not be very meaningful, this method is deemed to be reliable for analyzing trends among similar species. The populations indicate that the phenyl ring undergoes only relatively small changes in charge upon protonation or removal of an electron (or both) from the species. Most of the changes in charge occur at the two head-groups, the amine and the thiol. In the case of adsorption to particles, the electrostatic interactions that may lead to configuration changes from flat to perpendicular adsorption below the pzc and upon protonation of the amine are consistent with the charge redistribution obtained in these calculations.

To conclude this section, we note that a single silver atom is a poor representation of the particle. Further calculations to test the effect of metal-cluster size on the Raman frequencies and on charge distribution are required. The present results are used merely as an indication for the effect of the metal on the probe molecule. Furthermore, if a chemical charge-transfer mechanism is to be a contributing factor to the enhancement mechanism, determination of the excited states of the open shell species are needed as well. These will be further investigated in future reports.

Conclusions

Using the synthesis developed by Evanoff and Chumanov to produce well-characterized "naked" silver-particle suspensions and a probe molecule, *p*-ATP, of reasonably well-understood SERS enhancement mechanism we explored the changes that the particle and the probe undergo at various stages of the

Table 1. Mulliken Populations Summed over Groups of Atoms and Selected Vibrational Frequencies (with Their Corresponding Wilson Designations) Calculated for Representative Model Species

	$\text{H}_2\text{N-Ph-SH}$ (a)	$\text{H}_2\text{N-Ph-SAg}$ (a)	$\text{H}_2\text{N-Ph-SAg}^+$	$^+\text{H}_3\text{N-Ph-SAg}$	$^+\text{H}_3\text{N-Ph-SAg}^+$
Population:					
H/Ag on S	-0.06	0.16	0.20	0.50	0.36
S	0.03	-0.05	0.19	-0.48	0.39
Ph ring	0.36	0.34	0.56	0.43	0.63
$\text{NH}_2/\text{NH}_3^+$	-0.33	-0.45	0.05	0.55	0.62
Vibration:					
19b ($\nu\text{CC}+\delta\text{CH}$)	1427 (1423/1445)	1431 (1440)	1478	1420	1402
19a ($\nu\text{CC}+\delta\text{CH}$)	1496 (1490/1493)	1487 (1488)	1491	1469	1459
NH_3^+ umbrella				1502	1528
8b (νCC)	1575 (1572)	1563 (1573)	1498	1575	1543
8a (νCC)	1611 (1595)	1606 (1590)	1618	1588	1571

^a Experimental Raman frequencies from ref 21 are given in parentheses. ^b Experimental SERS frequencies from ref 21 are given in parentheses.

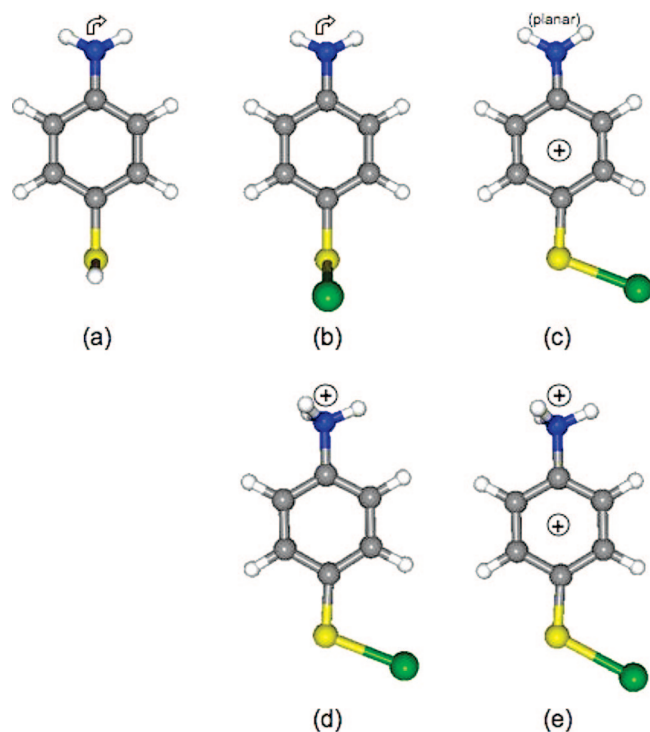
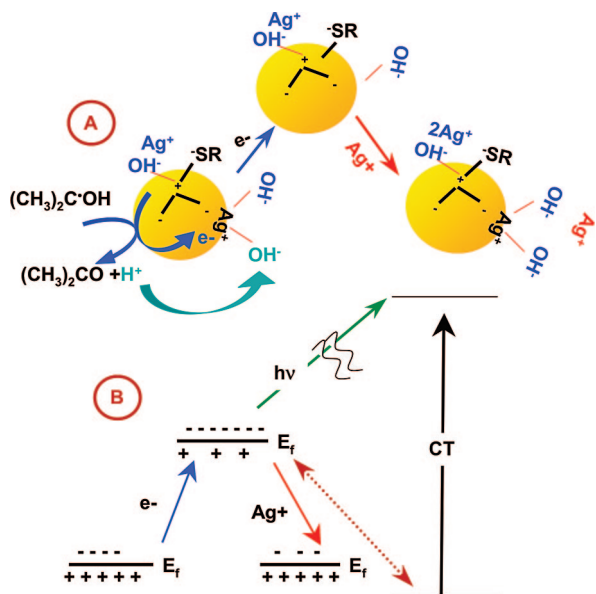


Figure 11. Optimized structures of the species in Table 1. (a) H₂N-Ph-SH, (b) H₂N-Ph-SAg, (c) H₂N-Ph-SAg⁺, (d) ⁺H₃N-Ph-SAg, (e) ⁺H₃N-Ph-SAg⁺. Blue = N, yellow = S; green = Ag.

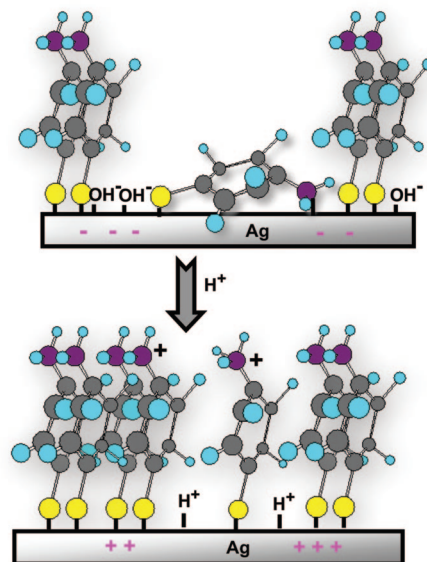
Scheme 1. (A) Changes in the Particle in Response to External Chemical Reactions; (Left) Electron Transfer Reduces Ag⁺ but Is Accompanied by Proton Transfer; (Right) Addition of Ag⁺; (B) Changes in Fermi-Level Energy in Response to the Chemical Processes Shown in (A)^a



^a Following ref 21, the dashed double-arrow indicates the energy-dependent vibronic coupling of the Fermi level with the ground state.

catalysis of hydrogen evolution from strongly reducing radicals. These changes are schematically displayed in Scheme 1A. Prior to catalytically evolving hydrogen, a preconditioning stage takes place, in which high enough overpotential accumulates on the particle. In this stage reduction of residual Ag⁺ ions initially occurs followed by accumulation of negative charges on the particle. During this stage clear changes take place in the SERS

Scheme 2. Change of *p*-ATP Orientation on the Particle as a Result of Crossing the pzc from Basic to Acidic pH^a



^a Gray represents carbon atoms, yellow - sulfur, blue - hydrogen, magenta - nitrogen.

spectrum of the probe. These changes are primarily assigned to the change in E_f , the energy of the Fermi level of the particles. Addition of silver ions decreases E_f , and injection of electrons raises it. When the source of the electrons is reducing radicals, as in the present case, proton release compensates the injection of electrons resulting in little effect on E_f . Lower E_f increases the vibronic coupling between the Fermi level and the ground state. Depending on the excitation wavelength, this may lead to an increase or decrease in SERS intensity via the resonance enhancement component of the charge transfer mechanism (Scheme 1B). The dependence of enhancement on the chemical potential, particularly on silver ion concentrations and pH, may at least partially explain the difficulties of recording consistent SERS spectra even for particles that were obtained from similar synthetic procedures.

Most interesting in the present context is the effect of independently changing the pH (in distinction from electron-injection coupled to pH change described above) on the SERS spectra and on the particle surface. The particles of this synthesis resemble metallic cores with thin hydroxide layers, probably of monolayer dimensions or less. The “as synthesized” particles are usually at basic pH, above the pzc at the pH 9–10 range. Neutralization of hydroxides at the surface has an effect on the Fermi level similar to the effect of the addition of Ag⁺ ions. Quantitatively though, this effect may be distorted by the effect of pH on solubility of the ions. Furthermore, as the pH decreases below the pzc and the surface becomes positively charged, concomitant protonation of the amine headgroup takes place. A possible interpretation is that those molecules that are adsorbed in a flat orientation change their adsorption mode to a perpendicular orientation, which results in observable increase in the in-plane vibrational modes. Alternatively, changes in the Fermi level may induce charge transfer from the molecule to the particle. Increasing silver ion concentration or acidity may

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increase the fraction of open-shell species on the particles, leading to changes in the SERS spectra and enhancement patterns.

The sequence of events that follows the absorption of radiation as they pertain to the catalytic process can then be outlined as follows: The initial reaction is injection of electrons that reduces silver ions and a parallel decrease in pH since protons are released by radical reactions with the particles. Reduction of silver ions then leads to little effect on the Fermi level. Enhanced SERS intensity at this stage is mostly due to the configuration changes outlined in Scheme 2. Alternatively, electron exchange between the molecule and the particle may cause similar spectral changes. When the reduction in silver ion concentration becomes the dominant effect and changes in pH are minimal (i.e., catalytic H₂ evolution dominates), the Fermi level rises, and eventually no SERS spectra can be recovered. At this catalytically cycling stage the overpotential on the particle is less than -0.45 V vs NHE. Finally, we note

that the use of a probe provides meaningful information on the particles, the probe itself, and their relative interactions. Information on the interaction of the reducing radicals with the particles is still lacking. Time-domain experiments are obviously required to address the interactions among these short-lived species.

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